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THE THEORY OF THE *Photographic* PROCESS

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VICE PRESIDENT IN CHARGE OF RESEARCH
AND DEVELOPMENT · EASTMAN KODAK COMPANY

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To SAMUEL E. SHEPPARD, D.Sc.,
in recognition of a collaboration in
research on the theory of the photographic process
which has continued for forty years.

PREFACE

During the last fifty years, scientific workers interested in the study of the photographic process have built up a fund of knowledge which is scattered through the literature in several languages and in a great diversity of journals. The purpose of this book is to provide a general handbook of the subject as a guide to the literature and as a summary of its conclusions.

Such an undertaking is possible only by the co-operation of a large number of specialists, and the author is fortunate in the generous assistance which he has received from his colleagues in the Kodak Research Laboratories.

The book as a whole owes much to Dr. K. C. D. Hickman and Mr. R. M. Evans.

Dr. S. E. Sheppard contributed much material to Chapters I, III, and IV. Chapter II was revised by Mr. A. P. H. Trivelli and Mr. R. P. Loveland; and Chapter III, by Dr. J. A. Leermakers. Dr. J. H. Webb added much to Chapters IV, V, VI, and VII. A considerable part of the Section on Development, including the whole of Chapters IX, X, and XII, was written by Dr. Arnold Weissberger. Chapters XIII, XIV, and XV were revised by Mr. J. I. Crabtree and Dr. W. Clark. Mr. C. M. Tuttle wrote part of Chapter XVII, and Dr. L. A. Jones revised the Section on Sensitometry and wrote Chapter XX. Chapter XXI was revised by Dr. F. H. Perrin; and Chapter XXII, by Dr. O. Sandvik and Mr. W. K. Grimwood. Chapter XXIII was written by Dr. L. G. S. Brooker and Dr. B. H. Carroll; and Chapter XXIV, by Dr. Brooker. Dr. Carroll and Dr. Leermakers revised Chapter XXV. Dr. E. E. Jelley contributed several sections of chapters.

The author is indebted to Dr. G. Kornfeld for much assistance in revision and, above all, to his secretary, Miss I. A. Schmitt. Acknowledgment should be made of the usefulness of K. V. Chibisoff's book, *Theory of the Photographic Processes*.

One omission in the book requires explanation. A book on the theory of photography should contain a chapter on emulsion-making, discussing various methods of procedure and their effect upon the finished product. The author's knowledge of this subject has been acquired in confidence, however, and he is not entitled to publish the material with the frankness which alone would justify any publication.

C. E. KENNETH MEES

ROCHESTER, N. Y.
July, 1942.

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INTRODUCTION

The photographic process involves the following operations: An image is formed by means of a lens upon a layer containing light-sensitive material. After exposure, the layer is *developed* by chemical treatment, and a visible image is produced. The unexposed and unchanged material is now removed by solution. This is termed *fixing* the image. The image so obtained is usually a *negative*, in which the bright parts of the original scene appear dark and the dark parts, bright. The negative is printed upon another light-sensitive layer, which, in turn, produces a visible image which is termed a *print*, or *positive*.

In this process, the colors apparent in the original scene are not recorded as such, but the negative and positive images represent them in monochrome.

Special processes can be used to produce photographs in color. These utilize a combination of monochrome processes by which the colors of the scene are reproduced by different proportions of three colors.

The *theory* of the photographic process involves a study of the nature of the light-sensitive layers used, of the factors which control their sensitivity to light, of the changes induced in them by the action of light, of the nature of development, and of the properties of the final image and its relation in tone values to the tone values of the scene from which it was produced.

In modern photographic processes, the light-sensitive material is almost always a compound of silver. Compounds of iron, chromium, and a few other metals are sensitive to light, as are certain organic compounds, such as the diazo compounds, which break down under exposure to light. Iron and chromium have been used extensively in the production of photographic prints; but the photographic process which is considered in this work depends upon the light-sensitivity of the compounds of silver, and the photographic materials discussed are those which are formed by the suspension of halides of silver in a layer of gelatin.

PART I

THE PHOTOGRAPHIC MATERIAL

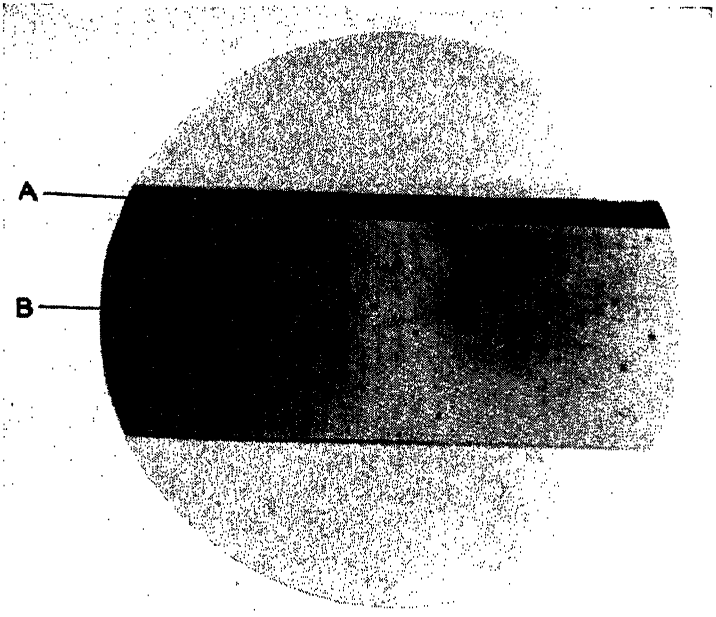

FIG. 1. Photomicrograph of cross section of portrait film, about ×1500. A, emulsion; B, support.

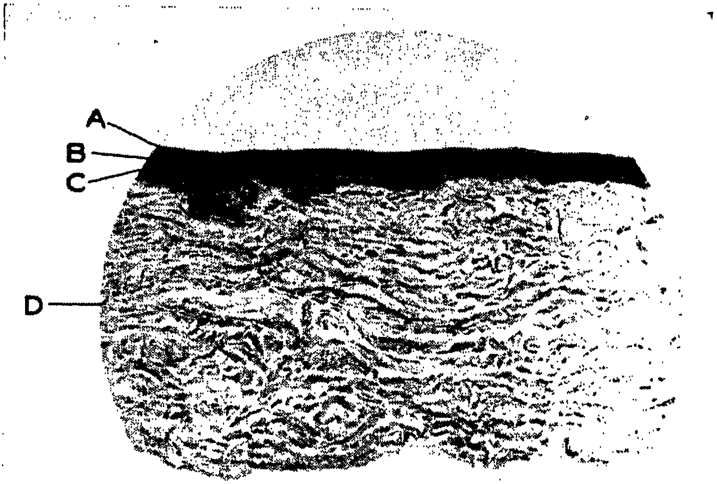

FIG. 2. Photomicrograph of cross section of bromide paper, ×1500. A, overcoating; B, emulsion; C, baryta layer; D, fiber.

CHAPTER I

THE LIGHT-SENSITIVE MATERIAL

Photographic materials are, in general, of two types: negative materials and positive materials, usually paper.

Both negative materials and photographic papers are made by coating an *emulsion* upon the base. Negative emulsions are suspensions in gelatin of silver bromide containing a little iodide, from which most of the soluble salts resulting from the precipitation have been removed by washing.

Paper emulsions may have the same constitution as negative emulsions, that is, they may consist of silver bromide free from soluble salts; but the emulsion of most photographic papers is composed of silver chloride or a mixture of chloride and bromide which has not been freed from soluble salts by washing.

The making of light-sensitive emulsions is an art belonging to the practice rather than the theory of photography. For an understanding of the properties of emulsions, however, a brief account of their preparation is desirable.

NEGATIVE EMULSIONS

In the preparation of negative emulsions there are three separate operations:

1. The emulsification and digestion (*ripening*) of the silver halide;
2. The freeing of the emulsion from excess soluble salts, usually by washing;
3. The second digestion (*after-ripening*), to obtain sensitivity.

Photographic emulsions are made from solutions containing generally 10 per cent or more of the soluble halide and silver nitrate. The gelatin used in emulsification is only a small part of that necessary in the finished emulsion. The addi ion of the silver to the bromide solution is made under fixed conditions of temperature and rate of addition to produce the dispersion required, and then the precipitated silver bromide is ripened by heat in the presence of a solvent until the processes of growth and of coalescence and recrystallization described later are completed. When this stage is finished, sufficient gelatin is added so that, on cooling, the emulsion sets to a firm jelly. It is then cut into small fragments, usually by squeezing through a grid under pressure; and the soluble salts, consisting of alkali nitrate produced from the reaction and excess of alkali halide, are removed by washing in chilled water until the diffusion is complete. Then the emulsion is remelted, usually with the addition of a further quantity of gelatin, and held at a moderate temperature until the after-ripening produces the required sensitivity and contrast.

The two stages of digestion differ not only in the effects which they produce but also in their functions. The first stage is intended to establish the grain distribution of the silver bromide, and this distribution is affected very little, if at all, in the process of after-ripening, as shown by Chibisoff and Mikhailova.[1] On the other hand, before washing, the emulsion has low sensitivity and very low contrast; and during the after-ripening the grains undergo profound changes in their reaction to light, owing to their acquisition from the gelatin of the sensitizing materials referred to in Chapter III.

1. EMULSIFICATION AND RIPENING

Inasmuch as this operation determines the distribution of grain sizes, the character of the emulsion is fixed at this stage. The silver nitrate solution is added to the bromide solution by running it through a funnel at a definite rate with a very considerable degree of stirring to prevent any great local excess of silver nitrate. The concentration of the alkali bromide in the solution must be of the order of 10 per cent or slightly higher. A lower concentration does not provide enough silver halide in the finished emulsion, while a much higher concentration causes difficulty from the formation of coarse-grain precipitates.

All negative emulsions contain some iodide. The amount varies from nearly zero to a maximum of about 10 per cent of the silver bromide present. Potassium iodide is usually added to the potassium bromide solution before precipitation, but it may be added during precipitation or ripening. The action of silver iodide in silver bromo-iodide emulsions is complicated. It produces finer-grained emulsions with higher speed and contrast, if the concentration is low.

In emulsification, only a small part of the total gelatin is used, the bromide solution containing usually from 1 to 5 per cent of gelatin, and this gelatin is selected for its protective ability rather than its possession of the photographic sensitizers necessary in the gelatin used later in the process; that is, the gelatin used in precipitation is generally of an inactive type and is also what is termed by the gelatin makers a "soft" gelatin—one of low melting point and generally low jelly strength.

There are two different types of emulsions: neutral emulsions and ammoniacal emulsions. In the case of the neutral emulsions, a large excess of alkali bromide is used to enable the Ostwald ripening and crystallization to proceed because of its solvent power for silver bromide. In the case of the ammoniacal emulsions, the ammonia may be added to the bromide solution; but it is more usual to employ what is termed a *converted* silver nitrate. This is prepared by adding ammonia to the solution of silver nitrate until the precipitate of silver oxide just redissolves in the excess of ammonia; the silver is then in the form of a complex ion with ammonia. Upon precipitation, the ammonia is released from the complex ion and is present in the emulsion. The temperatures used in making neutral emulsions are much higher than those which can be employed for ammoniacal emulsions; temperatures of the latter exceeding 50° C. are dangerous and very soon produce fog, while in the absence of ammonia, it is possible to precipitate at temperatures from 70° to 90° C. The higher the temperature and the slower the rate of addition of the silver nitrate, the greater the range of grain sizes produced and the larger the maximum size of grains. But the same result can be attained by long-continued ripening, so that an emulsion of large grain size and eventually of high sensitivity can be obtained either by adding the silver very slowly, and so building up large grains in the course of precipitation, or by adding the silver rapidly and obtaining a fine-grain precipitate, which is then allowed to recrystallize by digestion in the presence of excess of alkali halide or of ammonia. The rate of Ostwald ripening and of recrystallization, which controls the final grain distribution, depends upon the solubility of silver bromide in potassium bromide solution and in ammonia. The solubility of silver bromide in ammonia, in the presence of potassium bromide, has been studied by Lialikov and Piskunova.[2] They give the following table, from which it is seen that the presence of nitrate increases the solubility of the silver bromide during the ripening process:

TABLE I

Solubility of AgBr in 1 M NH_3 at 35°C.
Effect of KNO_3 and KBr

Without KNO_3 *Moles KBr*	*Without KNO_3* *Moles AgBr*	*With KNO_3* *Moles AgBr*
0.01	0.00134	0.00230
0.02	0.00084	0.00154
0.03	0.00066	0.00130
0.04	0.00054	0.00094
0.05	0.00047	0.00080
0.1	0.00033	0.00054
0.2	0.00033	0.00044
0.4	0.00038	0.00046
0.8	0.00059	0.00084
1.6	0.00248	0.00324

In the absence of ammonia, the solubility of silver bromide in dilute potassium bromide solutions is so low that the point of minimum solubility is difficult to measure. The minimum solubility occurs at a concentration of approximately 0.001 N, the initial depression of solubility presumably arising from the effect of the common anion on the dissociation equilibrium, while the increase of solubility with increasing concentration of bromide is due to the formation of complex ions. The solubility increases very rapidly, both with concentration of the soluble bromide and with temperature, so that at high concentrations and high temperatures it is sufficient to permit of rapid Ostwald ripening and recrystallization even in the absence of ammonia.

When an emulsion is formed by the slow addition of silver, the extent of after-ripening is of little importance because the recrystallization occurs largely during precipitation and there are few very fine grains to be dissolved and reprecipitated. On the other hand, if the emulsion is precipitated rapidly, a long digestion will produce the desired redistribution of grain sizes.

Broadly speaking, high-speed neutral emulsions used for negative work can be prepared by slow addition and long ripening at high temperatures and in the presence of ammonia at lower temperatures; while the lower-speed emulsions used for process work or the making of lantern slides or positive film are made with more rapid addition at lower temperatures, so that they show a more uniform and finer grain distribution than the high-speed emulsions.

After the emulsion is ripened, a considerable quantity of gelatin is added, usually bringing the emulsion up to a strength of about 10 per cent in gelatin. As already mentioned, the properties of this gelatin are of the greatest importance, since on them depends the sensitizing to be attained later. When the gelatin is dissolved, the emulsion is chilled as rapidly as possible and allowed to set to a firm jelly, after which it is cut into shreds a few millimeters in diameter.

2. THE WASHING OUT OF SOLUBLE SALTS

Photographic emulsions are washed between the ripening and finishing stages to remove the potassium nitrate and any excess of potassium bromide present during the ripening operation. The amount of washing can be fairly satisfactorily controlled by careful maintenance of the conditions of flow of water and its temperature, with variations in time of washing to secure optimum results.

3. THE SECOND RIPENING

The emulsion is melted for the after-ripening, and at this point the last of the gelatin is added if all of it has not already been used for setting. A photographic test of the emulsion as soon as it is melted will show that it is not only low in sensitivity but gives low contrast; but as it is held at a temperature of 50° C., or more, contrast and sensitivity increase very rapidly until, in ten minutes or so, the emulsion attains the normal contrast for that type of emulsion. Sensitivity will continue to increase for a time depending upon the whole structure of the emulsion and the gelatin used. Gelatins differ very much in their effect upon the rate at which sensitivity increases after ripening, and by adjusting the time of ripening identical results can be obtained with gelatins of widely different properties (Chapter III, p. 93).

After a limited time, usually less than an hour, the increase of sensitivity ceases; and, if the ripening is continued, the emulsion will, after a time, begin to show a serious increase in fog. The emulsion sometimes begins to show fog before the maximum sensitivity is reached, owing to the improper adjustment of emulsion precipitation and choice of gelatin. If an emulsion is insufficiently ripened, so that the maximum sensitivity is not reached before the after-ripening is stopped, the ripening is stated to continue during storage of the emulsion; and even if the emulsion is coated and dried, the coated material will continue to increase in sensitivity when it is kept. If, on the other hand, the emulsion is over-ripened near to the point of fogging, it will be unstable on keeping; and the coated material is likely to develop fog when stored.

A finished liquid negative emulsion contains about 6 per cent of gelatin (dry weight) and 4 per cent of silver halide. It is coated on the support to a depth of about 0.3 mm., from which it dries down to about 0.025 mm. in thickness. The coating on paper shrinks from about 0.1 mm. when wet to 0.04 mm. when dry. Negative materials, therefore, contain about 1.5 mg. of silver halide per square centimeter, and papers, about 0.5 mg. Cross sections of developed negative film and bromide paper are shown in Figures 1 and 2.

PAPER EMULSIONS

Most of the emulsions used for printing paper are unwashed. Chloride is used instead of bromide, and most or all of the gelatin is added at the beginning. The quality and sensitivity of such emulsions depend upon the formula, the gelatin, and the exact conditions of precipitation. The silver chloride is produced in a very finely dispersed condition and can be seen as distinct grains under only the highest powers of the microscope. Owing to the presence of the soluble salts, which may crystallize out on an impermeable support, unwashed emulsions can be used best with an absorbent support, such as paper.

The relatively rapid bromide papers used for enlarging are made with a washed emulsion of a slow negative type.

THE SILVER HALIDE PRECIPITATE

If a drop of diluted emulsion is examined under the microscope, the silver halide crystals will be seen to be well defined in form and to range in size from the limit of visibility to a maximum of perhaps 5μ in diameter, the average diameter for a rapid negative emulsion (Figure 3) being about 1μ. The photographic properties of the emulsion depend upon the composition and structure of the individual grains, upon their crystalline forms, and upon the conditions of precipitation, which produce grains of different sizes and distribution of size.* The presence of gelatin profoundly modifies the nature of the precipitate (Chapter III).[3,4]

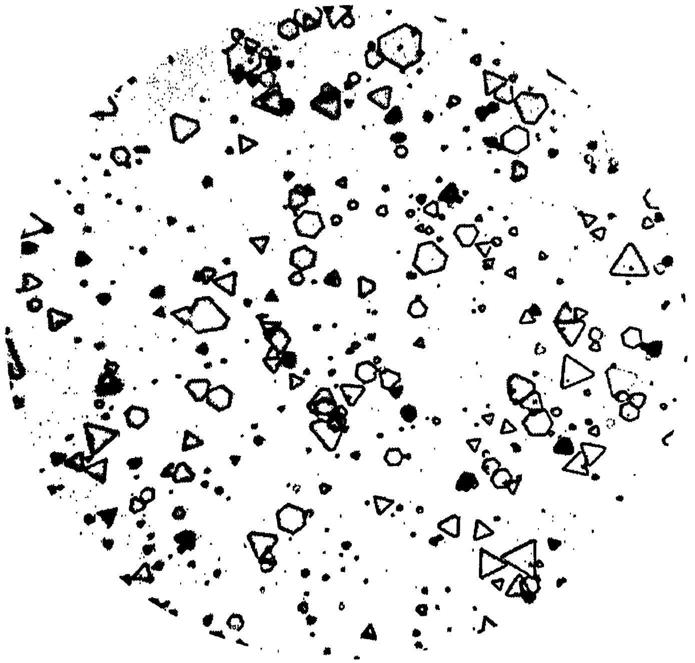

FIG. 3. Photomicrograph of the silver halide crystals of a negative emulsion, about ×2500.

The silver halides are among the least soluble salts known, and with silver thiocyanate and silver sulfide they form a series decreasing in solubility in the order: silver chloride, silver thiocyanate, silver bromide, silver iodide, and silver sulfide. The deposition of these silver salts from the double decomposition reactions is so rapid that the precipitate appears entirely amorphous. It was not until the X-ray analysis[5] of powders had been perfected that Wilsey[6] was able to show that the halides are always microcrystalline. Crystals which are visible under the microscope or even large enough to be seen by the unaided eye can be obtained by the use of substances which form soluble complexes with the silver halide, such as potassium bromide or ammonia. This makes possible the continued supply of silver and halide ions from a solution containing a very low concentration of the free ions. The crystals so obtained belong to the cubic system, but their external shape may depend upon the composition of the solution from which they are grown. With potassium bromide as the solvent, octahedral faces are produced, and the crystals present triangular and hexagonal outlines; with ammonia, octahedral faces are generally produced, but crystals with cube faces have been obtained.

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* If the diameters of all the grains in a given volume of an emulsion are measured and if the diameters are plotted against the frequency with which they occur, a distribution curve results which is not unlike that which could be deduced from the laws of probability (Chapter II).

If two solutions yielding a precipitate are mixed, the conditions of interaction will alter progressively from the moment the first drop of one meets the other. Though they contain equivalent quantities of salt in unit volume when they begin to mingle, the formation of insoluble product leaves the solutions weaker than before. Each succeeding element of precipitate, therefore, originates from a less concentrated medium and a medium growing richer in reaction products.

The environment during precipitation can be varied artificially. The solutions may be made to differ from each other in concentration, even though the quantities of salt involved remain equivalent, by dissolving one reactant in less water than the other. In this case, most of the precipitate is formed in contact with an excess of the more concentrated reagent. The effect is accentuated if precipitation is performed with solutions which are not equivalent; at the finish, the solid product is in contact with an excess of one of the reacting bodies.

All these conditions may arise during emulsion-making, and, although silver halide is produced in each case, the properties of this halide may vary appreciably. Why this should be so can be explained according to current theories of chemical combination and the structure of crystals.

In the latter part of the last century, acceptance of the law of *constant proportions* and the law of *multiple proportions* for the combining weights of the elements led to a simple mechanical conception of *valency*. One atom could unite with one, two, three, or up to eight atoms of another element, according to its valency. The compound was the sum of its molecules and its composition was therefore exactly that of the molecules. Silver and bromine being monovalent, the compound silver bromide in any quantity would consist of X silver atoms and exactly X, to a unit, bromine atoms. The combination between gram-atom masses of silver (107.88 gms.) and bromine (79.9 gms.), each containing, as now known, about 6.06×10^{23} atoms, would be pictured as the separate interlocking of silver and bromine atoms in pairs, each union being a separate event taking place without regard to the others in the neighborhood. Whether, therefore, there were an excess of a few atoms of either component left over in the general pairing would not seem to modify the nature of the product already formed. The excess would merely be rejected and left in the solution.

The researches of Werner and of Bragg and Bragg and the theoretical work of Bohr, Lewis, Born, Fajans, and others [7] have shown that this picture is insufficient. For salt-like compounds, the valence arm of the earlier chemists becomes a convenient abbreviation for forces generated by the interchange of electrons between combining atoms. In the solid and probably in the liquid states, such chemical combination is no longer considered a private affair, as between atom and atom; it is a group relation concerning colonies of atoms.

When silver bromide is precipitated from solution, the silver and bromine ions are not attached to one another in pairs, with the resulting molecules lined up to form a crystal, but are arranged in a symmetrical pattern in which it is impossible to say that any one bromine atom is the property of any particular silver atom. It is the reduplication of a vast number of silver and bromine ions in a regular three-dimensional mosaic or *lattice* which constitutes a crystal. Each crystal habit has its own lattice structure, in which the atoms are situated at definite distances and in definite directions from one another. If it cannot be said that the purpose of crystal habit is to afford each atom the greatest contact with the other component and the least possible contact with its own members, this, at any rate, is the effect achieved.

Wilsey's powder X-ray analyses of silver chloride and bromide have shown them to have simple cubic lattices; the sides of the unit pattern, a solid element of which is shown in Figure 4, have lengths of 2.78 A and 2.98 A, respectively. It is seen that each silver atom is surrounded by six bromine atoms, and each bromine atom by six silver atoms, the sets being disposed in a series of interpenetrating cubes. The valency is still unity, in that silver bromide is composed of equal numbers of atoms of silver and bromine. It is the *method* of attachment which is conceived to be different. If each atom cannot be said to be bound to its neighbors by six valence bonds in the place of one, it is at least held in position by a unit force exerted fractionally in six directions. The idea of aggregates of individual molecules thus gives place to that of the crystal itself as a giant molecule, which, owing to its regular structure, obeys the laws of constant proportions.*

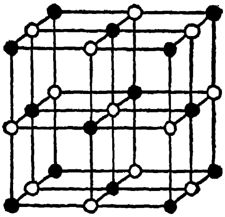

FIG. 4. Diagram of the cube lattice of silver chloride and silver bromide.

The theory of electrolytic dissociation has long suggested that, in solution, the components of *salt* molecules are separated or, at least, interchangeable. Silver bromide, though considered insoluble in water, does dissolve to a minute extent; and, since it is a compound of a metal with a strong acid, the part in solution is almost completely dissociated, thus:

$$AgBr \rightarrow Ag^+ + Br^-.$$

The process must be considered a dynamic one, however; the ions bombard the solid material which cannot further dissolve, displacing occasionally one or other of the components in the outer layers and reforming the surface with new members.

---

* This is only true for *ionic* crystals, such as silver bromide, and not for *molecular* crystals, such as those of most organic compounds, in which the molecule retains much individuality.

If, in the solid state, it is natural for the silver and bromide ions to remain stationed in a certain relative order, this is not possible in solution, owing to the freedom of movement in liquids. As the saturation point is passed, however, at a critical concentration a crystal begins to separate. Material continues to deposit until the amount of salt in solution has decreased to a new value, expressive of the fact that it is easier for ions to deposit once a nucleus has been provided. For the first act of crystal generation, a solution *supersaturated* as regards the crystalline salt is required. The reason for the easier deposition on a crystal already started is simple. In the center of a crystalline aggregate, each atom has its valency forces satisfied equally in each direction by ions of opposite sign. At the surface, however, this condition obtains only in those portions of the atoms facing inwards, and each one is left unsatisfied on the side towards the solution. The surface, therefore, is always acquisitive, first for ions of one sign, then for those of the opposite; and as long as the process of attachment takes place, the crystal grows. The limit of growth is reached when the loss of material to the solution is equal to the rate of deposition, which occurs when the solution is impoverished to the saturation limit. If one of the ions is then in excess, as if an extra quantity of a soluble salt containing the ion is added, the finished crystal will have attracted a layer of these ions to its entire surface, a layer which cannot be covered by ions of opposite sign because of their scarcity. Insofar, then, as the surface has an extra layer of one component, the crystal differs by this amount from the composition demanded by the law of constant proportions. In the large crystals of laboratory stock chemicals, the ratio of the number of atoms in the surface to those in the interior is so exceedingly small that little variation in composition is detectable. The fine precipitates met with in analytical work, however, are often found to contain more of one component than they should. The excess of precipitant may be occluded or adsorbed. The ratio of surface to volume is appreciable in this degree of subdivision, and the adsorbed ions alter the composition to a measurable extent. In the case of the thin platelike crystals which commonly occur in emulsions, calculations show that the excess of silver or bromide ions amounts to .03 per cent for grains 1μ thick (very large crystals) and .33 per cent for grains 0.1μ thick.

The case of silver bromide precipitated from silver nitrate and potassium bromide is typical: Let either component—for example, the potassium bromide—be in excess. At the beginning of precipitation, silver, potassium, bromide, and nitrate ions are thrown together. Solid silver bromide separates until substantially all the silver ions have been removed and leaves in solution an excess of bromide ions and a greater number of potassium and nitrate ions. The surface of the silver bromide now attracts these ions, the bromide and the nitrate tending to adhere to the outermost silver members of the lattice, while the potassium ions collect at the bromide members. But, of the three varieties in solution, only the bromide ions are common to the lattice and are of dimensions such that they fit in with the surface structure of the mosaic. Only these, therefore, can approach sufficiently intimately to be held. Since the ions are charged particles, the acquisition of a layer of bromide ions renders a crystal negatively charged. It has an affinity, therefore, for an equal number of positive ions, in this instance, potassium, from the solution; and the concentration of these increases in the neighborhood of the crystal surface until electrical equilibrium is established.

If attempts are made to wash or dry the crystal, the dynamic equilibrium of ions in the vicinity at once becomes static, each excess surface bromide ion attracting a supplementary potassium ion and attaching it permanently to an external layer. In chemical parlance, *the silver bromide has retained some potassium bromide in an adsorbed condition.* Particular stress is laid upon the fact that if one ion is adsorbed to a crystal, the companion ion is always concentrated in the neighborhood to an equivalent extent. There is a tendency in photographic and colloid literature to speak of adsorbed ions as though they were present without their consorts. This has arisen because, for practical purposes, if the crystal is in contact with a solution, it is only the attached members of the ion pairs which modify the surface. The conditions existing around a silver bromide crystal in a solution containing an excess of potassium bromide may be pictured diagrammatically, as in Figure 5. This shows the cubic face of silver bromide. The cubic faces are seldom found in photographic emulsions but are those considered by Fajans and Frankenburger in their interesting researches.[8] The faces developed by the octahedral crystals of a negative emulsion present a surface of ions all of one kind, as in Figure 6, or, if precipitation is performed in excess of silver nitrate, according to Figure 7.

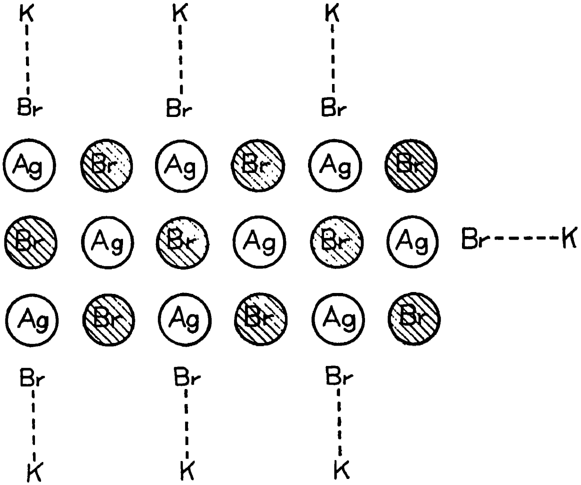

Fig. 5. Diagram of the silver bromide lattice showing potassium bromide adsorbed to cubic faces.

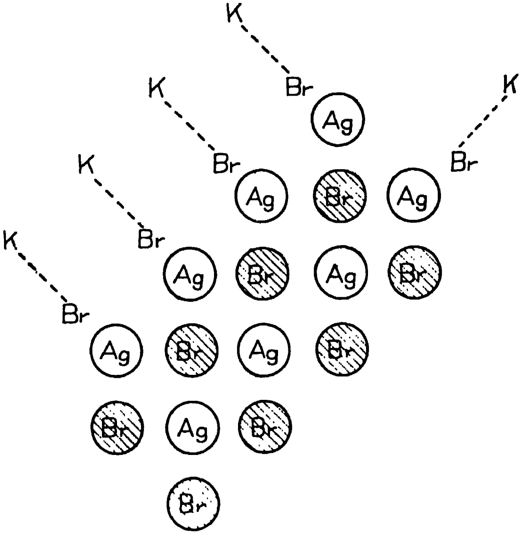

Fig. 6. Diagram showing bromide adsorbed to an octahedral face.

The companion potassium or nitrate ions of the adsorbed bromide or silver ions are individually free to move away and be replaced by others. The crystals can, therefore, be regarded as electrically charged towards other crystals should these approach. This electrification has important physical effects. The particles of a precipitate prepared in the presence of excess of one reagent repel one another since they are charged with the same ion. This prevents coalescence and gives rise to a colloidal solution if the crystals are small enough. The adsorbed ion has *peptized* the precipitate, and the solution remains cloudy and will not settle. If a suspension of an insoluble salt charged in this way is mixed with a suspension of a similar salt prepared in an excess of the other reactant, the particles of opposite sign attract one another, neutralization of charges takes place, and the material flocculates.

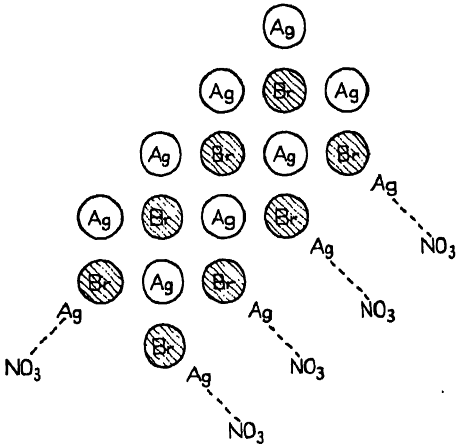

FIG. 7. Diagram showing silver adsorbed to an octahedral face.

Fajans and Frankenburger introduced a convenient terminology for these precipitates. When prepared with adsorbed silver ion, the silver bromide is spoken of as the *silver body;* with adsorbed bromide, as the *bromide body;* with OH^-, as the *hydroxide body;* and so on. The silver body and the bromide body have electric charges of opposite sign, so that they precipitate one another from colloidal suspension; and they differ chemically in all reactions in which surface phenomena are concerned. In particular, silver halide with adsorbed silver is instantly reduced to metallic silver by a developing solution and is also very rapidly discolored by the action of light. It is, therefore, used for the preparation of photographic materials on which a visible image is printed by continued exposure without development, as in the case of the printing-out papers coated with an emulsion containing silver chloride and silver citrate. On the other hand, silver chloride and bromide emulsions intended for development are always made by the addition of silver nitrate to a solution in which the free halide is kept in excess.

PRECIPITATION IN GELATIN SOLUTION

The precipitation conditions in emulsion-making are complicated by the presence of gelatin. Gelatin is perhaps the best *protective colloid* known. Its structure in solution is such that it prevents the formation of solid particles until an enormous degree of supersaturation has been reached. Furthermore, it protects the particles from flocculation or fusion with one another after they are formed. Its effect on the precipitation of silver bromide is very marked. Ordinarily, potassium bromide and silver nitrate in one hundredth normal solution yield a cloudiness immediately on mixing. In the presence of gelatin, even tenth normal solutions give a clear yellow colloidal suspension of silver bromide, which remains transparent for some time.

The photographic emulsion requires comparatively concentrated solutions of the reactants, and these produce the light-sensitive crystalline grains in two distinct stages: After mixing, there is great supersaturation, followed by the generation of an immense number of nuclei and the growth of these until supersaturation ceases. This is the first stage. The second, already mentioned (p. 5) as ripening, involves clumping and fusion and also the solution of the smaller particles and redeposition on the larger. Ultimately, well-defined crystals are produced which are visible under the microscope. Finally, these grains undergo coalescence and recrystallization. The existence of these three stages in the precipitation of silver bromide is confirmed by the work of Trivelli and Sheppard,[3] Sheppard and Lambert,[9,4b] and Chibisoff.[10]

The processes of *inception* and *growth* have been studied by Tammann [11] on melts and by von Weimarn [12] on solutions and have been shown to depend on such factors as viscosity, pressure on the medium, and the concentration of the reactants, as well as the solubility and latent heat of crystallization of the insoluble substance. The initial separation of the nuclei can be expressed by the general formula:

$$W = R\,\frac{\text{condensation pressure}}{\text{condensation resistance}}\cdot\frac{P}{S} = R\,\frac{Q - S}{S}$$

where W = velocity of condensation,
Q = total available molecules in solution,
R = a constant,
and S = normal solubility of large particles of precipitate.

Thus, the solubility of the just-separating nuclei at any moment is equal to the degree of supersaturation at that moment or equal to $Q - S$; P/S is the specific supersaturation. Actually, however, the ideal case does not occur; that is to say, the first period of crystallization by no means represents a simple vectorial condensation of molecules or ions but is in a large measure complicated by a series of other processes (dissociation and association, solvation and desolvation, etc.). In the expression for the velocity, therefore, the coefficient R stands for some variable factor embodying all secondary reactions which accompany the main process of formation of the crystalline lattice in the shape of separate hyper-ultramicroscopic particles.

In the case of interest here, the formation of the solid phase occurs, as already mentioned, as a result of the reaction of double exchange; ions of silver and of halide take part in the process of condensation. But most ions are in a hydrated state in the case of aqueous solutions, holding and orienting the water molecules which appear as dipoles surrounding the ions. Hence, for the ion to pass into the crystalline lattice of the nucleus of condensation, the energy of dehydration must be supplied. The energy necessary for this is derived from the attraction forces arising between oppositely charged ions and constituting ultimately the so-called *lattice energy*, U_0, *i.e.*, the heat released, while N (Avogadro's number) positive and negative free gaseous ions combine into a gram molecule of the corresponding crystalline assemblage. The balance of the lattice energy and the heat of hydration gives, according to Fajans, the heat of solution:

$$U_S = U_H - U_0.$$

Thus, from considerations of energy, a given chemical compound is the less soluble, and, therefore, the velocity of its condensation is the greater, the stronger the forces of electrochemical affinity between oppositely charged ions in comparison with the hydration forces, *i.e.*, the greater the lattice energy compared with the heat of hydration. The values, in calories, of the said magnitudes for silver halide salts are as follows:

	Silver Chloride	*Silver Bromide*	*Silver Iodide*
Lattice energy U_0	208	203	197
Heat of hydration U_H	192	183	170
Heat of solution U_S	−16	−20	−27

If for silver the heat of hydration is assumed to be U_H = 105 calories, its values for the ions Cl′, Br′, and I′ are 87, 78, and 65, respectively. Thus, much energy is obtained if the ions are packed in regular order to form a crystal, but only a little is obtained as heat of precipitation because a considerable amount of this energy is used up in dehydrating the ions. A discussion of the formation of the solid phase, starting with the condensation of nuclei from the supersaturated solution or during the reaction of double exchange, leads to the conclusions:

1. If the supersaturation of the solution is constant and the time of observation is sufficiently long, the sizes of individual crystals will be inversely proportional to the rate of condensation into nuclei; in other words, with increasing specific supersaturation, systems with increasing store of surface energy are obtained.

2. At a certain mean supersaturation, or in the case of double exchange reaction, with increasing initial concentration of the reacting substances, the degree of dispersity of the liberated solid phase passes through a minimum, the precipitate approaching then its crystalline state. At lower and higher concentrations, a tendency to form sols and gels, respectively, is observed. According to von Weimarn, the precipitated solid phase is obtained in a highly dispersed state under the following conditions:

(*a*) The dispersion medium has a negligibly small solvent action on the solid phase which is being formed;

(*b*) The solid phase is formed very rapidly;

(*c*) The concentration of reacting substances in solution is kept within definite limits.

The practical meaning of these rules is: that the less soluble the substance, the finer the precipitate; and that, with very insoluble substances, the particles can be made to grow only by renewing the generating agents. Growth may then occur on crystals already laid down instead of commencing around fresh nuclei.

RIPENING

That one particle may grow at the expense of another is well known. In the estimation of calcium as oxalate, for instance, the precipitate which is formed on the addition of ammonium oxalate and ammonia to the calcium solution is usually left to settle over night. This is not done only to obtain a clear, supernatant liquid, which must inevitably be disturbed on filtering, but to allow the crystals to coarsen for retention by the filter paper. If a gelatino-bromide emulsion is *ripened*, the same increase in crystal or *grain* size takes place. As these increases may occur long after the addition of reagents, the only source for the growth of the larger particles is the solution and ultimate disappearance of the smaller. Examination under the microscope shows that this is what happens. As the larger crystals grow, the smaller ones disappear. The underlying physical reason is not hard to see, though the exact mathematical analysis of the change requires more study. Solid matter in bulk is held together by the forces of cohesion, ultimately, therefore, by the forces between ion and ion in the space lattice. If a solid is reduced to powder, not only will frictional work be performed, which is dissipated in heat, but energy will be spent in tearing apart the lattice. The greater the subdivision, the greater the energy absorbed. This energy is potential and is stored at the broken surface whose atoms are only partly surrounded by compensating valence members. If all the particles of the powder could be brought close enough,* they would adhere and liberate the surface energy as heat. If, therefore, the powdered substance is placed in contact with a liquid which can dissolve it, even though slightly, the liquid also being in contact with the substance in bulk, the powder will dissolve and deposit on the compact portion because, in so doing, an exothermic change and a liberation of energy will be involved. The process is generally spoken of as *Ostwald ripening* because Ostwald,[13] in his investigations on the stable and metastable forms of mercuric oxide and iodide, was the first to show its significance.

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* Normally, this is prevented by films of gas and layers of oxide on the surfaces. Platinum and freshly cut rubber surfaces adhere because they do not suffer this contamination.

The general principles of the reciprocal growth and shrinkage of particles, particularly of droplets of liquid suspended in saturated vapor, have been stated by Helmholtz,[14] Hulett,[15] Jones,[16] Partington,[17] and Valeton;[24] and summarized by Nernst,[18] and Trivelli and Sheppard.[3]

The growth of a crystal is dependent on the supply of material at its boundaries. In mobile solutions, the removal of solute by deposition renders the liquid lighter and generates convection currents past the faces, the currents being swiftest where the growth is most rapid. The crystal is enabled to expand unhampered in each direction at rates proportional to the affinity for ions at the corresponding faces. The first effect of increasing the viscosity of the medium is to repress the convection currents and restrict the supply of food. This affects the quick-growing faces proportionally more than the slow ones, because they are dependent for increase on ionic bombardment, which is presumably constant for unit area irrespective of the face. The normal shape of the crystal should give place to one more spherical in contour, an assumption which is verified experimentally.

Occasionally, increase in viscosity produces the opposite effect. There are some instances where a crystal has been fed very slowly, so that there is at all times a limited amount of building material; yet the final shape, instead of being nearly spherical, has become intricately patterned. This condition is realized when a moist silver halide emulsion (coated on a support) is fumed with ammonia. The grains dissolve exceedingly slowly in the dilute ammonia solution and redeposit as parts of a large master crystal (Figure 8). This crystal is rarely homogeneous but contains many empty spaces, as though it were the mere skeleton of the desired form.

The forces operating in crystal growth are of two broad kinds: the tendency to *accumulate* and the tendency to *arrange*. Wherever accumulation is entirely unhampered, the ions can come together in a crowd and produce an aggregate of small, hastily formed crystals. Where the supply is slow enough to feed each crystal face at its own particular rate, then one perfect crystal results, of shape characteristic of the compound, for, although the supply is equally plentiful at each face, not every ion is attached at the first collision. The more quickly growing faces retain a greater proportion of the ions, and the differing rates of growth at the surfaces are an expression of the varying likelihood of an ion remaining in position after collision. A spherical crystal results if the supply rate is exceedingly slow, control being exerted by the extreme insolubility of the substance in the solution under consideration, so that the latter is always slightly supersaturated. Every ion hitting every face is

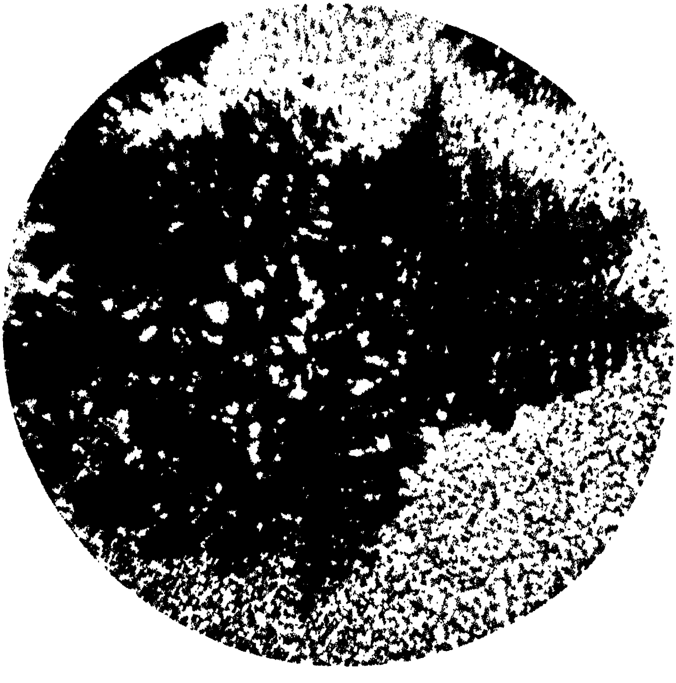


Fig. 8. Photomicrograph of silver bromide aggregate recrystallized by ammonia fuming, about ×15.

retained; but since there is (by definition) no evaporation, each ion must stay where it arrives.

Only if the supply of material is small but the solution less than saturated, as in the ammonia fuming referred to, can the arranging forces outplay the accumulative, for here ions deposited at positions not ideal for crystal habit can be re-evaporated before they are covered by new arrivals and can redeposit in more favorable regions. This transportation does not of necessity take place through the solution but may occur by means of a monomolecular adsorption layer which moves rapidly along the crystal surfaces. Evidence for the existence of these adsorption layers on solid surfaces was given by Volmer.[19] Since they tend to evaporate most quickly from the least acquisitive faces and deposit on their more greedy neighbors, a crystal of many branches and hollow interspaces results. The tips of the branches are the fast-growing faces, and the sides, the slow-growing.

The limitation of food supply and, thus, of crystal growth in the presence of dissolved gelatin never, of course, takes the path peculiar to the ammonia-fuming conditions. The grains merely become more regular. If an attempt is made to replace warm gelatin solution by another colloid of equal viscosity, it will be found that the precipitate of silver halide is not modified to the same extent. Gelatin exerts an especial power as a protective colloid, for it can totally inhibit crystallization as well as merely suppress growth. It is shown later that gelatin, even in dilute solution, has probably a fibrillar structure. A precipitate must, therefore, not only obtain sufficient material to grow; it must orient itself and its additions against the walls of the structure, while transportation through an adsorbed layer is blocked by the adsorbed gelatin. An obvious deduction, and one substantiated by experiment, is that regular crystalline precipitates can be obtained only when the gelatin solutions are stirred. The structure is mechanically broken (and probably instantly mended), and the crystals are nourished by forced convection currents. Trivelli and Sheppard[3] give a graph, reproduced in Figure 9, showing the effect of increasing gelatin concentration on the dispersity and grain size of silver bromide precipitates. In the particular conditions which exist during emulsion-making, the gelatin gives uniformity of growth to the grains instead of encouraging the large dendritic forms.

The work of precipitation of the solid phase on the faces of a growing crystal is expressed by the volume of the solid substance which is being precipitated from the solution per unit time on each face, and this volume is evidently proportional to the surface energy of a face. If F is the area of a face, V the volume of the substance precipitated per unit time, and K the capillary constant, the relationship is $V = q \cdot KF$, where q is a proportionality coefficient. Therefore, $v = V/F = qK$, that is to say, the thickness V/F of the layer deposited on the face per unit time, which expresses the velocity of growth v of the face, is proportional to the capillary constant of the given face. Experiments on the regeneration of crystals which grew irregularly or were deformed by heating the mother solution show (1) that the velocities of growth of different faces of a crystal are unequal and (2) that the face of greatest velocity of growth surrounded by other slowly growing ones tends to be excluded from the contour of the crystal. Thus, in growing crystals, the faces of slow growth are developed most, *i.e.*, those upon which a smaller amount of substance is being deposited per unit time. Rapidly growing faces may in time completely disappear from the crystalline polyhedron, being converted into edges or solid angles which indicate the directions of most rapid growth. The differ-

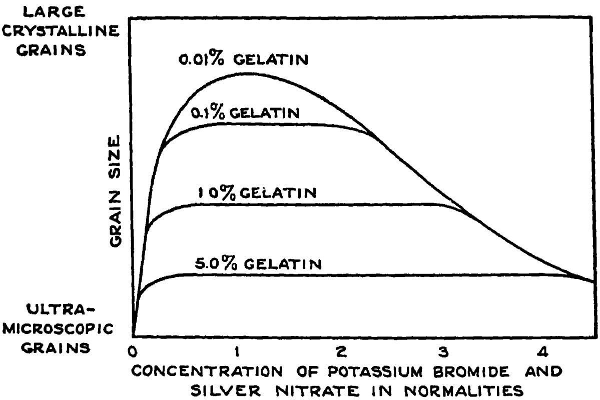


FIG. 9. Curves showing the dependence of grain size of the precipitate on the concentration during precipitation.

ence in rate of growth of the crystal faces is obviously due to the difference in their capillary constants. On the other hand, since during the growth of a crystal the faces of large capillary constant, *i.e.*, of great surface energy, disappear from its contour, it may be concluded that the most stable form of the crystal will be that to which corresponds a contour consisting of faces of minimal values of surface energy. The form of crystal which, under given conditions, is the most stable is called the *equilibrium-form*, *i.e.*, that which during the whole time of growth of the crystal remains similar to itself. This form may be different according to the conditions of crystallization (such as the supersaturation of the solution, impurities, etc.). If, for example, the growing crystal is placed in a solution of a different degree of supersaturation, its original form will be changed owing to the retardation of growth of some faces and the acceleration of growth of others.

Gibbs, Curie, and Wulff[20] state that the most stable form is that to which, for a given volume of the crystal, the smallest surface energy corresponds. Thus, the growth of a crystal in the mother solution is associated with a change of its surface energy; and, for a given specific distribution of capillary constants among the several faces, the growth of a crystal follows that form for which its total surface energy will be a minimum. This statement is known as the *Gibbs-Curie-Wulff principle of minimal surface energy*. It can be expressed by the equation

$$E = K_1 \cdot F_1 + K_2 \cdot F_2 + K_3 \cdot F_3 + \cdots + K_n \cdot F_n,$$

where F_1, F_2, F_3, $\cdots$ F_n are the areas of the faces of the crystal, to which correspond the capillary constants K_1, K_2, K_3, $\cdots$ K_n, while the total surface energy, E, for a given volume, V, of the crystal has to be a minimum.

The crystals observed in the photographic emulsion generally belong to the octahedral class of the regular system, although cubic forms are found.[21] The particular subclass is the dyakis-dodecahedral, concluded to be so from the study of growth rate at the different faces. The actual shape of the crystal can vary enormously, depending upon whether growth takes place equally in three dimensions or is restricted to two or even one dimension. The first gives prismatic grains which appear dark under the microscope; the second, plates; and the third, needles. All th variations may be considered derived from a regular octahedro by differential growth or extension of the faces. Let a regula octahedron rest on paper; then, the shadow in parallel projectio of the internal area bounded by traces of all its edges is a regula hexagon, as in Figure 10, and the eight facets are discernibl

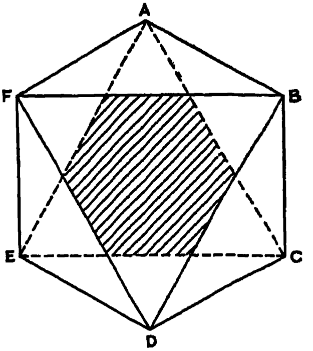


FIG. 10. Diagram of the projection of a regular octahedron showing the generation of a regular hexagon.

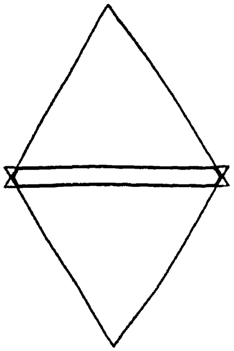


FIG. 12. Diagram of the generation of a needle-shaped crystal.

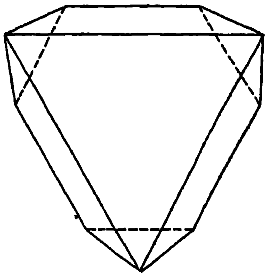
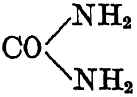


FIG. 11. Diagram of the generation of an equiangular, scalene hexagon.

after a little study. Thus *BDF* is one face; and *BCD*, another. If the rate of growth of all the faces is the same, the crystal increases in size but remains a regular octahedron. If, however, a pair of opposite faces, such as *BDF* and *ACE*, have one rate of growth, which is less than that of the other three pairs, a plate in the shape of a regular hexagon is formed. If, in addition, the three faces *ABF*, *BCD*, and *DEF* have a rate of growth different from that of their opposites, *CDE*, *AEF*, and *ABC*, the shape is that of an equiangular hexagon having alternate sides short and long. In the limiting case, a triangular contour results (Figure 11).

The point is that the areas of the faces in the fully developed crystal are inversely proportional to their rates of growth. Those faces which acquire material most quickly progress outwards, stretching and enlarging neighboring faces, while they themselves keep small. A needle is produced when growth is suppressed at all but the two basal surfaces. These grow in opposite directions, producing a long crystal which is reinforced with but little side expansion (Figure 12). More complicated needle growths are known.

It has been assumed that the development of crystal faces is dependent on their power of accumulation relative to that of their neighbors; but this law, enunciated by Lehmann,[22] does not hold good for the growth of certain forms, notably for octahedral plates with ikositetrahedral and dyakisdodecahedral skeletons. This is because secondary reactions come into play. It is known from X-ray photographs that common salt, NaCl, has the same lattice structure as silver chloride, AgCl;[23] yet when salt is crystallized from plain water, cube-shaped crystals form. This is in contrast to silver chloride, which occurs in an emulsion in octahedra. For a crystal to exhibit large cubic faces, growth must take place at the octahedral faces, since it is the faces which grow least that are extended sideways and that generate the largest areas. The quick-growing octahedral face is that on which all the external ions are of one sign, in this case, either Ag or Cl. It is, therefore, strongly charged positively or negatively. Such a surface exerts a powerful attraction on all ions of opposite sign, that is, on one half of those in solution. The cubic face, with its alternate structure, offers an equal 50 per cent chance of attachment to a bombarding ion; but, because of the alternations, the sphere of attraction diminishes very rapidly with the distance from the surface. It is slow-growing, therefore, and the face which persists in the normal crystals of common salt.

Valeton [24] showed that if much urea is placed in the salt solution, the sodium chloride separates as octahedra in the same manner as the emulsion grains in ammoniacal ripening. This is attributed to the adsorption of the strongly polar NH_2 groups of the urea,  $CO\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}$, to the octahedral faces, leaving the cubic faces free to grow. Sheppard suggests that the customary ammonia and excess KBr would play a similar part in emulsion-ripening by forming complexes of the type

$$[K]^+[AgBr_2]^-; \quad [K]^+[Ag_2Br_3]^-; \quad [Ag(NH_3)_2]^+[Br]^-$$

which are adsorbed to the octahedral faces. Further, gelatin containing $-NH-$ and $-NH_2$ groupings may play a similar role.

It has been pointed out by Jelley * that in consequence of the symmetry of the face-centered lattice of silver chloride and silver bromide, all the octahedral faces should have the same capillary constant, and the Gibbs-Curie-Wulff equation becomes

$$E = K(F_1 + F_2 + F_3 + \cdots + F_8),$$

which is a minimum when $F_1 = F_2 = \cdots = F_8$; that is to say, when the crystal is a regular octahedron. That the individual octahedral faces differ so markedly in rate of growth, even on very small crystals, indicates that the growing faces have a polarity not possessed by the crystal as a whole. Substances present in the solution in which the crystals are growing should likewise be adsorbed equally on all the octahedral faces. Jelley has prepared color photomicrographs of the reflection interference colors of silver bromide crystals, which show clearly that the opposite faces are not always parallel to each other but may be inclined by as much as 4°. This indicates that the rate of growth of a single face may vary from point to point.

In addition to the normal growth of the grains during precipitation and the Ostwald ripening, which occurs when the emulsion is digested in the presence of a solvent for silver bromide, there is possible a further modification of the grains by recrystallization and coalescence.

The process may be illustrated by the diagrams shown in Figure 13, taken from the paper by Sheppard and Lambert.[4b]

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* E. E. Jelley, private communication.

In Ostwald ripening, each particle is surrounded by an electrostatic double layer which consists of imperfectly oriented ions of the solid and ions of the solubilizing potassium bromide. These ions are more or less hydrated as they are more or less oriented. The electric moment of the hydrated ion depends upon the number of water dipoles surrounding the ion in a presumably monomolecular sheath. It is this moment that attracts and fixes the ion in the crystal lattice, thereby determining growth.

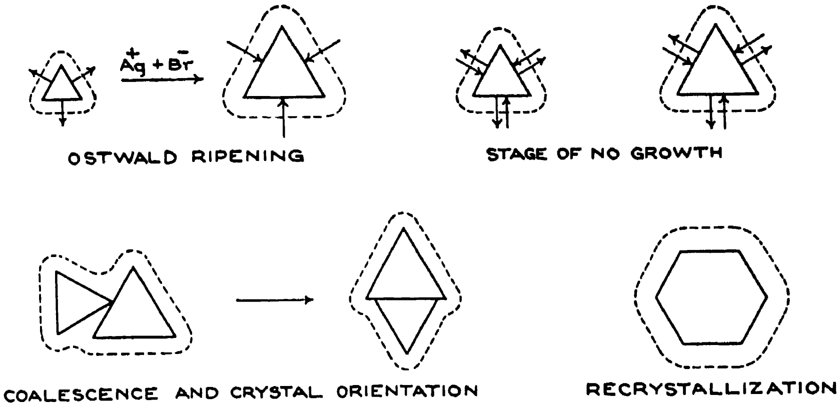
$\overset{+}{Ag} + \overset{-}{Br}$
OSTWALD RIPENING
STAGE OF NO GROWTH
COALESCENCE AND CRYSTAL ORIENTATION
RECRYSTALLIZATION

FIG. 13. Diagram of the processes of ripening, coalescence, and recrystallization.

During Ostwald ripening, there is in principle a transfer of water from the growing grain to the dissolving grain, so that they are kept apart by the neutral atmosphere thus created; and very few collisions result in coalescence. If, however, the double layers become similar in character with respect to the hydration of the ions, as they do as the process continues, coalescence will occur much as for two similar liquid globules; and the double layer of each grain is ruptured to form one layer about both grains. Finally, molecular orientation sets in since the double layer does not hinder such a process; and there is a tendency to decrease the surface, thus giving a single large crystal.

The general law of growth for the grains from the data of Sheppard and Lambert has the form $-dn/n = k\,dt$, where n is the number of grains in a given class in time t and k is a constant dependent on the concentration of soluble bromide. It can be shown that *n* is related to other parameters of the grains, such as their projective area and radius, from which the size-frequency relations are derived.

MIXTURES OF SILVER HALIDES

The presence of foreign or complex ions is not the only extra factor affecting growth and crystal habit. The use of mixed halides can produce a similar result. Silver bromide and chloride are isomorphous, both crystallizing under photographic conditions in octahedral forms of the cubic system. Since the bromide ions have a larger volume than the chloride, the lattice of silver bromide is larger than that of the chloride. In mixed crystals, the chloride lattice is strained and enlarged in proportion to the bromide content, but there is little tendency to alter the external shape. Silver iodide, however, exists in two allotropic forms, both of which differ from the crystals of bromide and chloride. One allotrope belongs to the hexagonal system, with the ions arranged in a hexagonal lattice, while the other belongs to the cubic system, as the bromide and chloride do. However, the lattice structures differ in an important respect, because, whereas the sets of silver and bromide or chloride ions can be considered as normal *interpenetrating* face-centered cubes, the silver and iodide ions are arranged in *staggered* face-centered cubes. Crystallizing silver bromide with silver iodide, therefore, involves a struggle on the part of the iodide not only to enlarge the lattice but actually to alter its form.

To obtain emulsions of high sensitivity and freedom from fog, a proportion ranging from 1 per cent to 5 per cent of silver iodide is used in the silver bromide. Wilsey [25] showed that this crystallizes as a solid solution with the bromide and enlarges the lattice without altering its structure. If, however, the amount of iodide is increased, not only is the lattice further enlarged, but, at a concentration between 15 per cent and 40 per cent of silver iodide, a new crystalline phase having one or both of the iodide lattice structures appears. It is not possible at present, according to Wilsey, to determine by X-ray analysis exactly where the change occurs. However, from the study of other properties of the iodo-bromide emulsion, a very fair guess can be made.

A silver bromide emulsion is cream-colored; an iodide, a pale yellow. Inclusion of a little iodide in the bromide does not alter the color proportionally in the direction of the yellow but discolors it to a deeper tint, amounting almost to orange with 30 per cent iodide. Further addition again lightens the color. Huse and Meulendyke [26] prepared and examined photographic emulsions containing bromide coprecipitated with varying quantities of iodide. Inclusion of the smallest quantity extended the sensitivity to light from the violet into the blue by an amount corresponding to the extension in optical absorption, *i.e.*, to the yellowing induced in the emulsion. The extension is progressive up to about 30 per cent, and then at 32 per cent a completely new spectral distribution of sensitivity appears and becomes more and more defined as the 100 per cent pure iodide region is approached.

Renwick [27] and his co-workers give results of experiments in which they found that homogeneity of the fully developed crystals within the emulsions which they made was not affected by the manner of addition of the iodide. Since silver iodide is the least soluble halide, it does not seem likely that it would dissolve and become incorporated with silver bromide precipitated later. Renwick obtained, however, identical emulsions whether he used preformed silver iodide or merely soluble potassium iodide.

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CHAPTER II

THE SIZES OF THE SILVER HALIDE GRAINS

The sizes of the crystalline grains of photographic emulsions vary through a wide range. Lippmann [1] made extremely fine-grained emulsions by mixing together quickly, and at as low a temperature as possible (about 35° C.), solutions of silver nitrate and potassium bromide, to each of which half the necessary gelatin had been added. These emulsions, still known by his name, are transparent when first mixed, the precipitated particles being submicroscopic in size. If they are allowed to stand (at 35° to 40° C.), they become opalescent and, finally, opaque; but even then the particles are not visible in the field of the microscope. When photographed by means of the electron microscope (Figure 14), they appear similar to the grains of

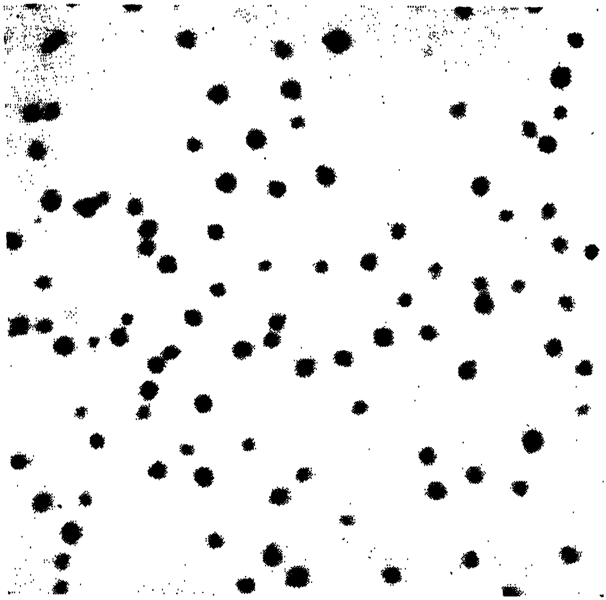

FIG. 14. Silver bromide grains of a Lippmann emulsion, photographed by the electron microscope. ×50,000.

ordinary emulsions, with a diameter of approximately 10 to 50 millimicrons. On the other hand, it is not difficult to make emulsions in which triangular tablets as large as 20 microns per side and needles 50 microns in length are formed.

A systematic study of the sizes of the silver halide grains in negative emulsions was made by Bellach and Schaum.[2] Outlines of the grains were drawn on graph paper by means of a reflecting system, and the surface extension and the greatest diameter were measured. The diameters of the grains were found to vary from 1½ to 3 microns, which agrees well with previous micrometric measurements by Kaiserling and Eder.[3] Bellach's observations were repeated by Sheppard and Mees,[4] who confirmed the general observations that the diameters of the silver bromide grains in a fast emulsion range from 1 to 3½ microns. They noted that the sizes of the grains in such an emulsion are distributed over a greater range than those in slow plates. In 1915, Mees [5] suggested that the different grain sizes and the photographic properties of an emulsion are related, emphasis being placed on the significance of the distribution of the grain sizes in the study of photographic emulsions.

The study of the grains of emulsions began to assume considerable importance after 1920, as a result of the investigations of Svedberg [6] and Slade and Higson,[7] when it was realized that not only does the sensitivity depend upon grain size but also the shape of the characteristic curve and such sensitometric characteristics as are involved in development. They found that the grains of an emulsion with high contrast are of approximately one size. Svedberg studied the distribution of the sizes of grains which become developable by exposure of one-layer grain plates and found that a quantitatively determinable relation exists between grain size and sensitivity. As Toy [8] showed, however, grains of the same size may differ in sensitivity.

Investigations of relations between size-frequency and sensitometric characteristics must be based upon statistical considerations,[9] and the determination of the size-frequency curve of the grain distribution of an emulsion is therefore important. The counting and measurement of grains as small as those of photographic emulsions are difficult tasks and required the development of an elaborate technique. Attempts have been made to use a mechanical method involving grain separation by sedimentation or centrifuging, but the results have not been satisfactory for the determination of grain-size distribution curves. The method is useful, however, for preliminary separation of the different grain sizes of an emulsion into fractions of smaller and larger average grain sizes. Renwick and Sease [10] used it to show that in silver bromo-iodide emulsions the larger grains contain more silver iodide than the smaller ones.

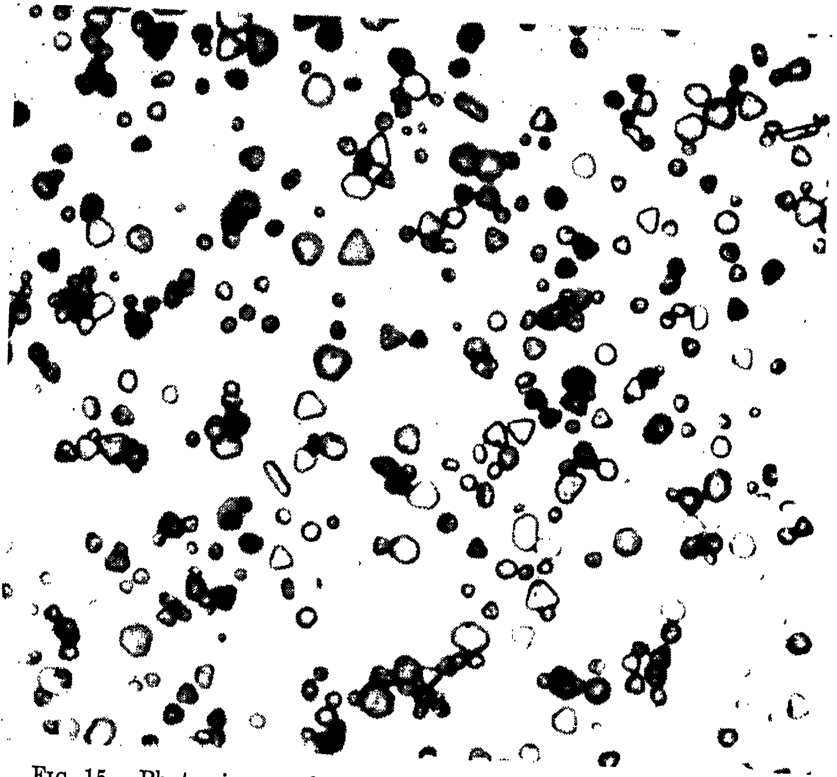

Fig. 15. Photomicrograph of silver halide grains in a photographic emulsion. ×2500.

The direct optical method using a microscope of high resolving power has been developed into a very useful and practical system of investigation. By it, the first distribution data were compiled by Wightman and Sheppard,[11] who made their measurements with the camera lucida, drawing the outlines of the grains on paper and measuring the projective area of the grains with a planimeter. The advantage of this method was its simplicity.

Photomicrographs of the grains reveal well-defined crystals separated by clear spaces, as shown in Figure 15. Trivelli applied photomicrographic methods to the measurements of grain sizes using a microscope equipped with an aplanatic condenser of 1.4 N.A. and an oil-immersion apochromat $f = 2$ mm. of 1.3 N.A. With a Homal IV ocular, which is a negative lens system suitable for projection of the image, a relatively large field of sharply focused grains can be obtained from smears. For fine-grain emulsions, higher resolution is required. Trivelli and Foster[12] used ultraviolet radiation of 365 mμ wave length from a mercury arc with a suitable filter. This gives a theoretical resolving power of 0.13 micron. The method is suitable for routine work and is used for emulsions having especially fine grain, although more time is consumed in the photography. The grains of some photographic emulsions are too small to be resolved in this manner; in fact, the grains of a Lippmann emulsion are barely visible as specks of light under dark-field illumination of especially high aperture. In the electron microscope, however, the limit of practical resolution is much less, probably of the order of 5 millimicrons. The particles of a Lippmann emulsion are easily photographed, and some preliminary size-frequency analyses have been made.[13] An example is shown in Figure 16. The number of grains measured (118) in this case

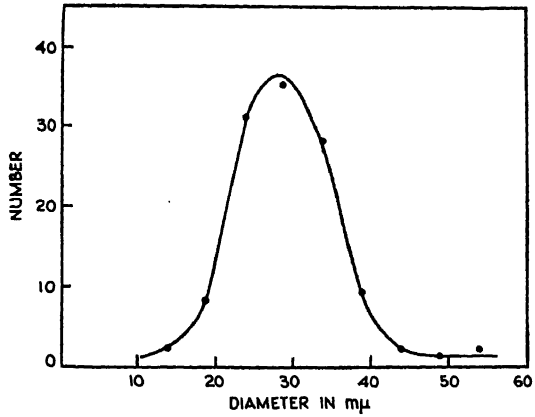

FIG. 16. Size-frequency analysis curve of the grains of a Lippmann emulsion.

is too small to determine definitely whether the distribution is the same as that in ordinary emulsions, but the normal probability curve has been used. The distribution is more symmetrical than is usually found in fine-grain emulsions, which agrees with the hypothesis [14] that the original particle size distributions produced by precipitation follow the LaPlace-Gaussian law and are changed by growth to the skew form.

The usual procedure for the determination of the size-frequency distribution in an emulsion is as follows: The grains are photographed at a magnification of 2500 diameters,* and the negative is again enlarged four times by projection. The actual measurements are thus made from pictures enlarged 10,000 diameters. Every centimeter measured then corresponds to one micron of the grain diameter. At this magnification, the outlines of the grains appear blurred, because the limit of resolution of the optical system has been exceeded, as shown in Figure 17. The measurement of the images is facilitated, however. The unit of size which is of importance for silver halide grains is the area, on which the light-collecting power depends. In the early work on the subject, the sizes of grains were expressed in terms of their diameters, but this has the disadvantage that the areas of grains of the same diameter will vary if they differ in shape.

In the bulk of an emulsion, there are many millions of grains, and between the limits of the smallest and the largest there is every possible size. For convenience, the grains are described here as falling into a relatively small number of classes.† The classes are broad, so that sufficient grains may be measured for a truly representative count without an undue increase in labor. On the other hand, accuracy demands a narrow band to prevent important variations within one class from being overlooked. The effect of doubling the number of classes on a distribution curve having a sharp maximum, which indicates a preponderance of grains of a certain size, is shown in Figure 18. The curve for larger classes is indicated by square points connected by a dashed curve; that for the half-size classes, by circular points connected by the solid line.

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* For general routine work, an oil-immersion objective of 1.25 N.A. used with a blue filter is satisfactory provided the grains are appreciably larger than 0.2 micron in diameter.

† Grain size expressed as the mean class size is, then, the statistical variable.[15]

Trivelli introduced the method of measuring by special rules which at once distribute the different grain sizes, regarded as circles, into the several classes. The number of grains per cubic unit of emulsion was determined by counting the grains per square unit surface of quantitatively controlled coatings which contained only one layer of grains. The inherent errors in the method are not great if from two to three thousand grains in an emulsion are measured.

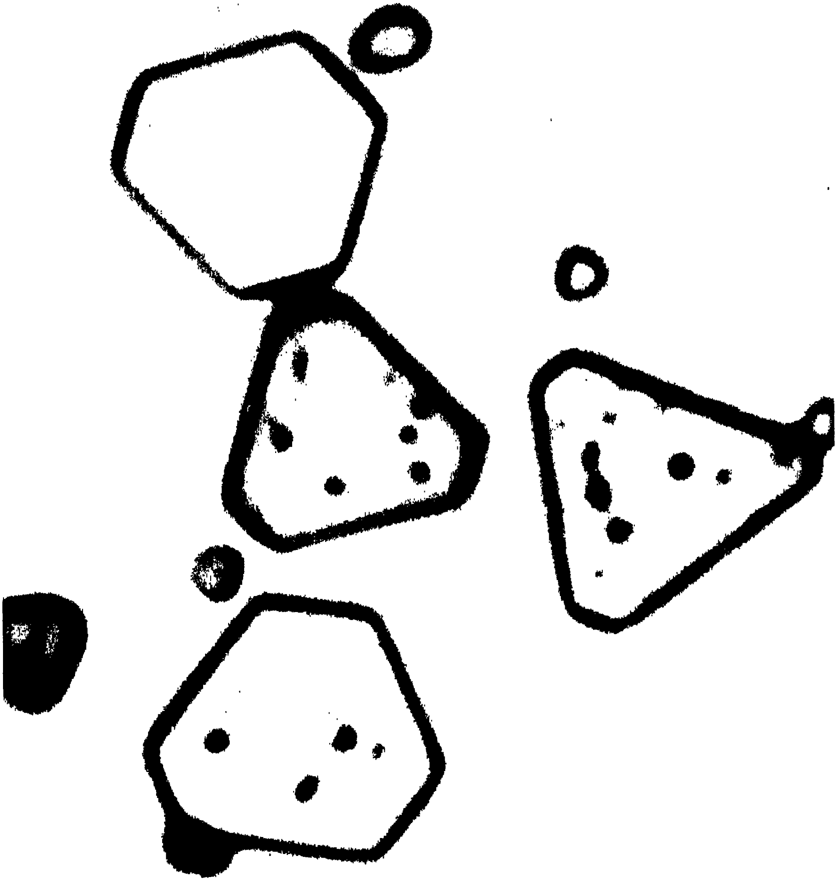

FIG. 17. Photomicrograph of silver halide grains from a photographic emulsion. × 10,000.

R. P. Loveland improved the methods to obtain higher accuracy, which enables size-frequency curves to be obtained with a smaller number of grains and shortens the time required to produce such curves. Loveland's technique represents the latest phase in the determination of size-frequency curves and will be described fully. As Figure 15 shows, the grains have different shapes. In the majority of cases, the images of the grains are circles,* triangles, or hexagons. Rectangular grains occur rarely.

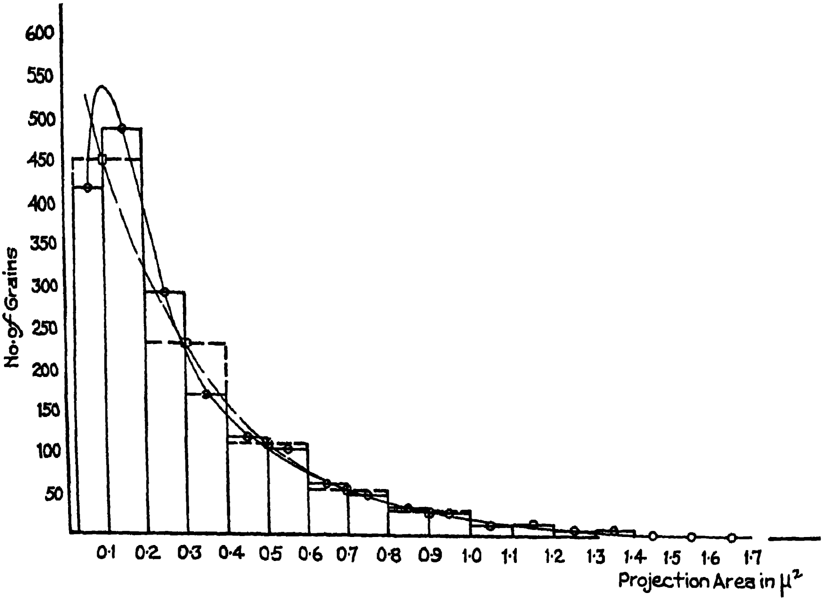

FIG. 18. Size-frequency curve showing the effect of doubling the number of classes.

Loveland, therefore, used different rules for the various shapes of grains, which are reproduced in Figure 19. These rules are calculated from the following formulas. If A is the projective area of the grain and d is the diameter of the circular grains,

$$d = \frac{2\sqrt{A}}{\sqrt{\pi}} = 1.12838\sqrt{A}.$$

If h_Δ is the altitude of the equilateral triangle,

$$h_\Delta = \sqrt[4]{3}\sqrt{A} = 1.31607\sqrt{A}.$$

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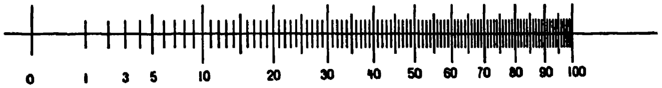
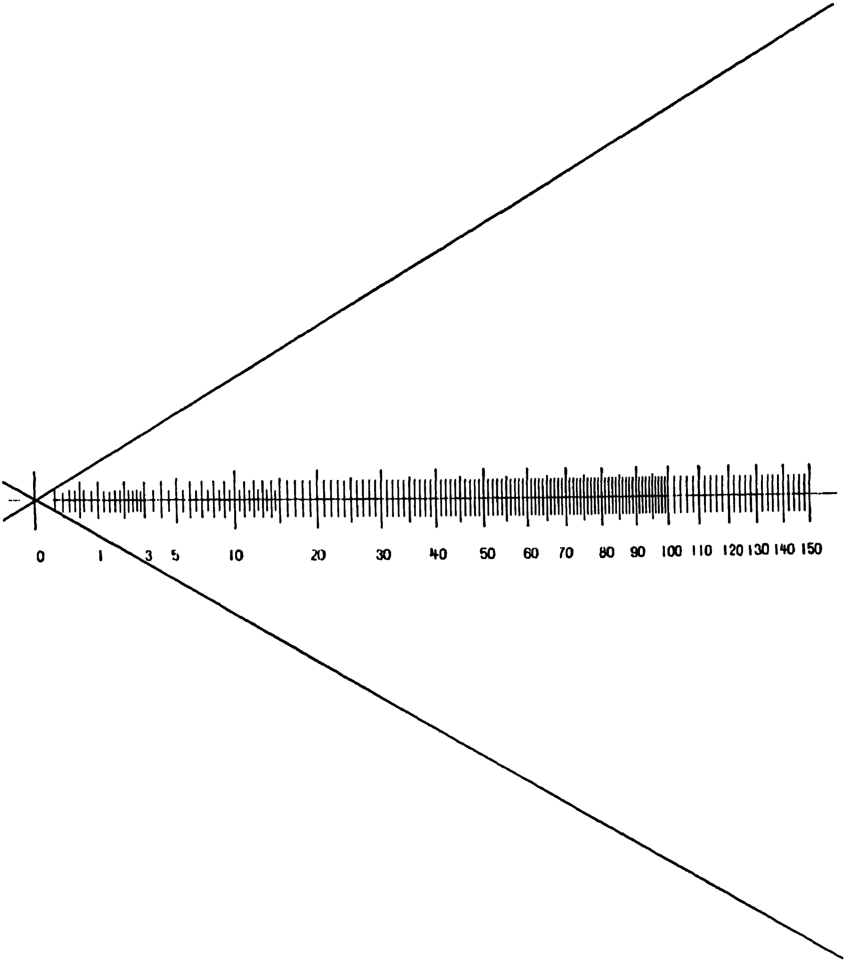
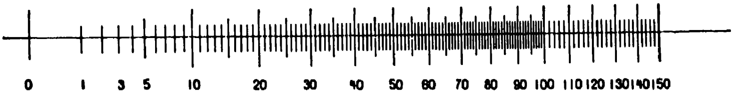
* These are chiefly the smaller grains, their apparent shape being due largely to the failure of the optical resolving power.



a, rule for the measurement of circular grains. ×2.



b, rule for the measurement of triangular grains. ×2.



c, rule for the measurement of hexagonal grains. ×2.

Fig. 19

If h_0 is the altitude of the hexagon,

$$h_0 = \frac{\sqrt{2}}{\sqrt[4]{3}}\sqrt{A} = 1.07457\sqrt{A}.$$

Taking the width of the classes as 0.1 square micron and expressing A in those units, a table can be compiled for the upper limit values of the classes, from which the rules can be drawn. Data for forty classes are given in Table II. The majority of commercial emulsions can be studied satisfactorily with these.

TABLE II

Class	A	d	h_Δ	h_0	*Class*	A	d	h_Δ	h_0
1	0.1	0.3568	0.4162	0.3398	21	2.1	1.6352	1.9072	1.5572
2	0.2	0.5046	0.5886	0.4806	22	2.2	1.6737	1.9521	1.5939
3	0.3	0.6180	0.7208	0.5886	23	2.3	1.7113	1.9959	1.6297
4	0.4	0.7137	0.8324	0.6796	24	2.4	1.7481	2.0388	1.6647
5	0.5	0.7979	0.9306	0.7598	25	2.5	1.7841	2.0809	1.6991
6	0.6	0.8740	1.0194	0.8324	26	2.6	1.8195	2.1221	1.7327
7	0.7	0.9441	1.1011	0.8991	27	2.7	1.8541	2.1625	1.7657
8	0.8	1.0093	1.1771	0.9611	28	2.8	1.8881	2.2022	1.7981
9	0.9	1.0705	1.2485	1.0194	29	2.9	1.9216	2.2412	1.8299
10	1.0	1.1284	1.3161	1.0746	30	3.0	1.9544	2.2795	1.8612
11	1.1	1.1835	1.3803	1.1270	31	3.1	1.9867	2.3172	1.8920
12	1.2	1.2361	1.4417	1.1771	32	3.2	2.0185	2.3543	1.9222
13	1.3	1.2866	1.5006	1.2252	33	3.3	2.0498	2.3908	1.9521
14	1.4	1.3351	1.5572	1.2715	34	3.4	2.0806	2.4267	1.9814
15	1.5	1.3820	1.6118	1.3161	35	3.5	2.1110	2.4621	2.0103
16	1.6	1.4273	1.6647	1.3592	36	3.6	2.1410	2.4971	2.0389
17	1.7	1.4712	1.7159	1.4011	37	3.7	2.1705	2.5315	2.0670
18	1.8	1.5139	1.7657	1.4417	38	3.8	2.1996	2.5655	2.0947
19	1.9	1.5554	1.8141	1.4812	39	3.9	2.2284	2.5990	2.1221
20	2.0	1.5958	1.8612	1.5197	40	4.0	2.2568	2.6321	2.1491

The rules can be drawn on paper and photographed with a fine-grain high-contrast emulsion coated on optical glass. They are mounted in a metal frame with a magnifying glass, and the rules for circular and triangular grains are used in most cases. Each shape of grain, considered in terms of its projective area—the circle, triangle, and hexagon, respectively—has its own component size-frequency distribution. Although the three overlap, the maxima and, therefore, also the "tails" of the curves occur at successively larger sizes on the scale in the order named above.

The rule for circular grains, as shown in Figure 19a, consists of a numbered scale, the numbers indicating the upper limit of the classes. If, for instance, a grain diameter fits between zero and a point between 5 and 6, the grain belongs in Class 6. If the diameter fits between zero and a point between 4 and 5, the grain belongs in Class 5. Usually, two diameters of the grain at right angles to each other are read, and an average of these two readings is taken for the class size.

For the measurement of triangular grains, the rule (Figure 19b) is placed over the grain so that the two sides of the triangle fit along two sides of the grain. The third side can then be measured by the scale in the same way as with the circular rule. The three corners of most of the triangles are truncated. In that case, the altitude of the missing part must also be read. The rule is then shifted, so that the apex is at another missing section. Again, both altitudes are read, and so on. The average of the readings of the three altitudes minus the total of the three missing portions gives the class size of the grains.

Hexagons are measured in three different directions (Figure 19c), and the average of the three altitudes is used. After the grains are classified, the total of those in each class is counted.

The determination of the size-frequency distribution of the particles of a specific emulsion is described here as an example of the method used in the Kodak Research Laboratories. A typical data sheet is shown as Table III. In this case, 1096 grains were measured and classified. The number of grains actually measured as belonging to the first class is 222. Here a fundamental difficulty in the microscopic method is encountered. The actual distribution of particle size probably extends to molecular size, which can be considered to be zero size with the units in use. However, no particles below microscopic resolution are included in those measured. The fraction of the true total number and the fraction of the size-distribution curve obscured in this way may vary from a negligible proportion to the major portion in different cases. The number of grains actually in the first class size, *i.e.*, all those present in the sample whose projective area is below 0.1 square micron, is estimated by extrapolation of the curve through the points plotted on double logarithmic paper * (Figure 20). This method is used because the apparent distribution is considerably simplified on such graph paper, particularly by the disappearance of an inflection point and, as discussed below, some criteria of its correct shape have been discovered. In practice, the curve is extended

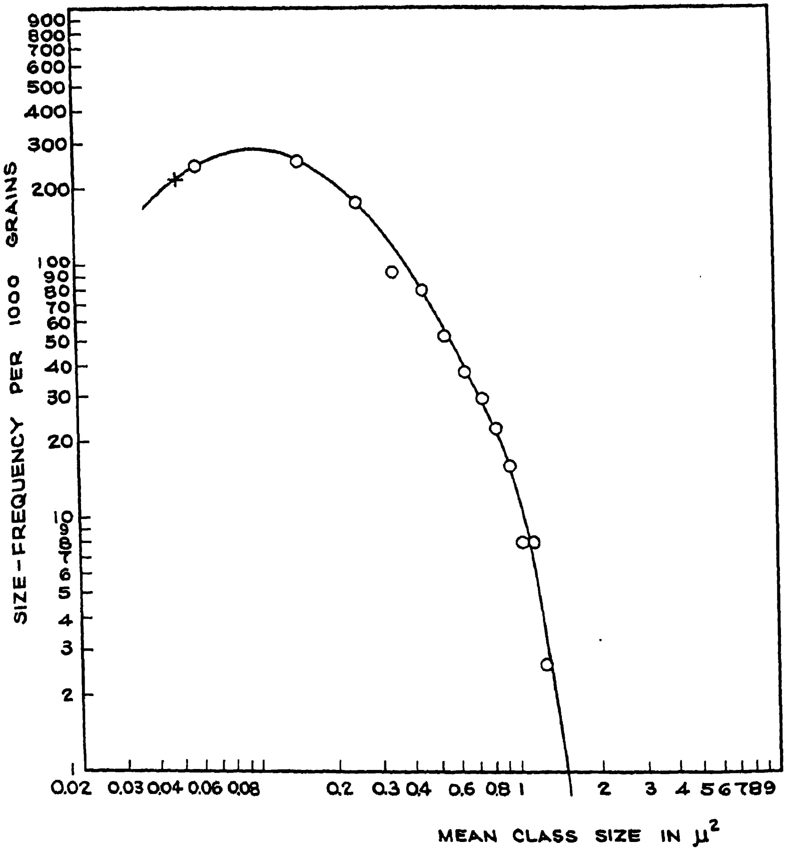


Fig. 20. Size-frequency curve plotted on double-logarithmic paper.

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* In plotting the data on any graph, account should be taken of the fact that the number in the first class as directly obtained (222 in this case) represents only the number whose sizes range from the lower limit of resolution (0.02 μ^2) to the upper limit of the first class (0.10 μ^2) and, hence, makes this class uniquely narrower than the others. The observed frequency of 222 must be multiplied by the factor $\frac{\text{standard class width}}{\text{variant class width}} = \frac{0.1}{0.08} = \frac{5}{4}$. The result, 279, is the number plotted *at the mid-point of the narrowed Class 1*, *i.e.*, at the value $x = 0.06\ \mu^2$. This is a purely graphical correction and should not be used in computations.

from $x = 0.06$ to $x = 0.05$; this extrapolation is preferable to the neglect of the error. Moreover, it furnishes a better estimate of the true total number of grains in the whole distribution. This, then, is the first step in the reduction of the data. In this case, the estimated number of grains in Class 1 is 240 (see Table III).

TABLE III

	Class	x	*Freq. observed*	y_0	Σy_0	xy_0	x^2y_0
Meas. for graph extrap.		0.06	222				
	1	0.06	279				
		0.05	240	215.440	215.440	10.772	0.539
	2	0.15	289	259.425	474.865	38.914	5.837
	3	0.25	192	172.352	647.217	43.088	10.772
	4	0.35	104	93.357	740.574	32.675	11.436
	5	0.45	88	78.995	819.569	35.548	15.996
	6	0.55	59	52.962	872.531	29.129	16.021
	7	0.65	42	37.702	910.233	24.506	15.929
	8	0.75	33	29.623	939.856	22.217	16.663
	9	0.85	25	22.442	962.298	19.076	16.214
	10	0.95	18	16.158	978.456	15.350	14.583
	11	1.05	9	8.079	986.535	8.483	8.907
	12	1.15	9	8.079	994.614	9.291	10.684
	13	1.25	3	2.693	997.307	3.366	4.208
	14	1.35	1	.898	998.205	1.212	1.637
	15	1.45					
	16	1.55					
	17	1.65	1	.898	999.103	1.482	2.445
	18	1.75	1	.898	1000.001	1.572	2.750
	Σn		1114	1000.001		296.681	154.621

In this table, x represents the projective area of the grains in each class as mean class size in μ^2; y_0 is the observed number of grains in each class; Σy_0 represents the accumulated size frequency; xy_0 is the total projective area of all grains within a class size; x^2y_0 is a term used in the evaluation of dispersion (p. 50).

The data resulting from the actual measurement may be given in the form of a column of figures or a series of individual points that represent the number of grains occurring within the limits of the successive classes of size (Figure 18). Then the problem is to determine the most probable form of the actual distribution of the sizes of the particles as a smooth curve for a great number of grains and, for purposes of comparison and calculation, to express this distribution by the best possible set of simple numbers, such as the average particle size, $\bar{x}$, and the spread or dispersion around that size. All size-frequency distributions are, therefore, put on the same relative basis of a total number of grains of 1000 by multiplying by the number fraction $\frac{1000}{\text{total number in sample}}$. The number of grains in Class 1, as estimated, is used to determine the total number of grains in the sample, *i.e.*, 1114 for the example given above.

The accumulated size-frequency, Σy_0, is also calculated by simple addition. This represents the fraction of the grains whose size is below that of a given size, x_l, and is always plotted against the upper limit of the class sizes instead of the midpoints shown in column 2.

The most probable continuous curve through the observed points can be determined mathematically.[14a] This is equivalent to finding the distribution that would occur if an infinitely great number of grains could be measured as a sample.

In the early work on size-frequency carried out in connection with the study of photography, the size-frequency distributions of the grains of all photographic emulsions were arbitrarily divided into two groups, according to whether it was considered that the symmetrical bell-shaped curve of the Laplace-Gaussian *frequency* function,

$$Y = Ae^{-k(x-\alpha)^2}\Delta x, \tag{1}$$

or the extremely skew, L-shaped curve of the simple exponential function,

$$Y = Ae^{-kx}\Delta x, \tag{2}$$

should be applied to them. In these equations, Δx represents the class width of the size units used in the measurements, which is normally constant. The method of least squares was used in fitting the data. Further investigation resulted in the development of a moderately skew type of function that has seemed to have a close correlation with the properties of the particle size distributions of photographic emulsions, and in every case it fits the data much better than either of the other two forms, namely:

$$Y = Ae^{-k(\log x-\alpha)^2}\Delta x. \tag{3}$$

In the first instance in which this equation was used, a high maximum, not predictable by the data, occurred in the curve. The grain-size distribution was remeasured, using one half the previous width of class size, with consequent greater accuracy. The newly determined curve fitted closely that previously determined, including the high maximum.[14a] A slightly different form of equation 3 is

$$Y = A'e^{-k(\log x - \alpha')^2}\frac{\Delta x}{x}, \tag{4}$$

which can be shown to be identical with the form (3) except for values of the constants A and α; in fact, Loveland and Trivelli showed that the distribution functions (3) and (4) are special cases of the more general form,

$$Y = Ax^n e^{-k(\log x - \alpha)^2}\Delta x, \tag{5}$$

where n could be made any positive or negative integer by a mere change of the constants A and α. This unique property of the formula means that whether diameters, areas, volumes, or weights were measured, the distribution law would be the same, only the value of the constants being made different by a change of variable $t = cx^n$ in each case.

In a mathematical study of botanical distributions, Kapteyn and van Uven [16] assumed that all distributions are *normal* (accurately described by the Laplace-Gaussian function) at first, and that the relationship of the final distribution to that of the error function is a measure of the growth, which, without some predominating influence, would remain of the same normal form. Among other equations for representing the final size-frequency curves for their botanical distributions, they mention the form (4), which is readily shown to be the normal distribution in terms of $\log x$. This distribution indicates, according to their theory, that the distribution is a result of growth proportional to the size attained at any given instant. On the basis of their theory, this distribution would certainly appear reasonable for a chemical precipitate.[14a]

The origin of such size-frequency curves was explained by Sheppard and Trivelli.[14b] It seems to lie in the distribution of the velocities of ions and molecules in the reaction solution. According to Maxwell, such velocities are distributed according to the normal probability law, which also holds for the velocities of the Brownian movement of the particles formed first. It may, therefore, be assumed that, at first, the same size distribution exists for the silver halide particles. This is determined by the probability of collisions between ions, between ions and particles, and between particles. The particles grow proportionally with the number of collisions, which is proportional to their size. The result is a skew size-frequency curve (p. 38).

This mathematical form was found to express satisfactorily the size-frequency curves of a number of emulsions; but, more usually, it was found that the distribution curves were composed of segments with distinct breaks or discontinuities, each one of which had the above form. Such distribution can only be represented by a mathematical series, and a series was applied to them with this same function,

$$Y = \frac{k}{\sqrt{2\pi}} e^{-k(\log x - \alpha)^2} \Delta x,$$

as the generating function. This was done by the statistical method of least squares. While the results were excellent, the time and labor consumed were prohibitive, and a faster method was sought.

A graphic method was found, based on the fact that when a smooth curve representing some arbitrary function is drawn through a series of points on the locus of another function, if a mathematical transformation is made, the curve may no longer seem to be a good fit for the points. For instance, after the transformation, the points might lie along a straight line and the curve obviously be an arc, or vice versa. A true fit would cause the curve to follow the shape of the points through all transformations. The simplest method of making such transformations is to plot the points of the observed size-frequency distribution on the several types of graph paper required and draw the curve through each in such a way that they are mutually consistent and a good fit in each case. The work is facilitated by choosing transformations that simplify the shape of the size-frequency curve.

If the particular function discussed above is plotted on double-logarithmic paper, its graphic representation becomes an inverted parabola, whereas if the normal function is plotted on semilogarithmic paper, its locus becomes a straight line. This last operation can be performed in one simple step by plotting the accumulated frequencies (such as column 5 in Table III) on semilogarithmic probability paper. As stated above, in only a few cases are the size-frequency distributions of the crystals of photographic emulsions accurately represented by a single such function, *i.e.*, a single parabola or straight line; but very often they are represented by two or more such curves joining rather sharply (Figure 21). Moreover, segments fitted by a straight line on the semilogarithmic probability paper must give a parabola on the double-logarithmic paper. In general, the smaller frequencies in the "tail" of the size-frequency curve are best smoothed or graduated from the double-logarithmic graph, and the higher frequencies, from the straight arithmetic plot (Figure 22, curve A), except that the double-logarithmic graph is valuable in determining the position of the maximum. The various frequency constants are then calculated in the usual manner,* using both the original data, such as that given in Table III, called the "observed constants" and designated by the subscript o, and also the data from points taken from the curves to give the "calculated constants" designated by the subscript c. The data of most interest are:

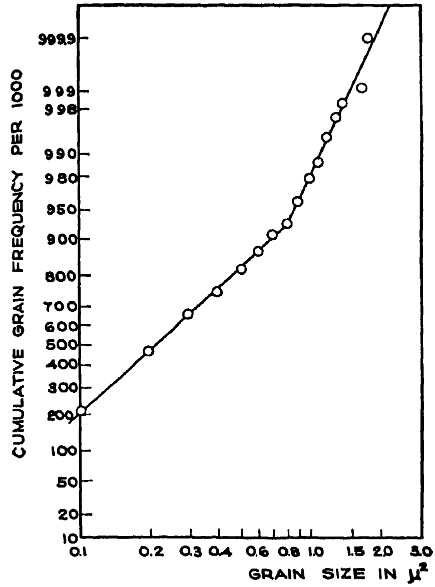

FIG. 21. Curve of normal function on semilogarithmic paper.

1. Average particle size $= \bar{x} = \Sigma xy/\Sigma y$, where $\Sigma y = n$. n is the total number of grains determined by the method discussed on page 46. In the case of the example presented there,

$$\bar{x}_{\text{obs.}} = 0.30\ \mu^2,$$
$$\bar{x}_{\text{calc.}} = 0.29\ \mu^2.$$

---

* Statistical forms for this are given in the *Handbook of Mathematical Statistics*, H. L. Rietz and members of Committee on Mathematical Statistics, Houghton Mifflin Co., New York, 1924.

2. Dispersion, σ, = $\sqrt{(\Sigma x^2 y / \Sigma y) - \bar{x}^2}$.

In the example:

$$\sigma_{\text{obs.}} = 0.26\ \mu^2,$$
$$\sigma_{\text{calc.}} = 0.24\ \mu^2.$$

3. The ratio 100 $\sigma/\bar{x}$ is sometimes called the *coefficient of variation*, C_v.

4. The median, x_{me}, is that size below and above which there is an equal number of grains. It is sometimes of value because, unlike the average, it is not materially affected by haphazard occurrence or absence of very large grains in the "tail" of the frequency distribution. It can be found graphically from the graph of the accumulated frequencies or by interpolation between the two adjacent values in the frequency table.

More closely related to the photographic characteristics of an emulsion than the size-frequency distribution of its individual grains is the total projective area offered by all of the grains of each size, since the latter is a measure of the relative importance of each size in contributing to the total projective area of the silver halide. This total projective area per class is also a distribution curve to be plotted against the grain size, x, and is represented by curve B in Figure 22. It is always determined when a size-frequency analysis of a photographic emulsion is made. The ordinates of curve B are calculated simply by multiplying each ordinate for curve A by its corresponding abscissa value ($Y = xy$). The area under this curve is an important constant, the total area of silver halide presented to the light per 1000 grains or per unit area of the photographic plate, according to the method of sampling. This, of course, is only strictly so when there is no shadowing or interreflection; but among emulsions having the same shape of curve, the area is approximately proportional to the total surface of the halide.

For the determination of other characteristics of the structure of the emulsion, it is necessary to know the *number of grains* per cubic centimeter of emulsion. This is measured independently. The necessary amount of emulsion is weighed out and diluted to 250 cc. with gelatin solution; 5 cc. of this diluted emulsion are coated uniformly on a 2″ × 5″ slide of high-grade plate glass. After drying, the plate is examined under high-power magnification with dark-field illumination. The ocular of the microscope is provided with a rule of square units. Each square covers a known section of the field so that, after the number of grains in several of these squares is counted, the total number N of grains per cubic centimeter of emulsion can be calculated.

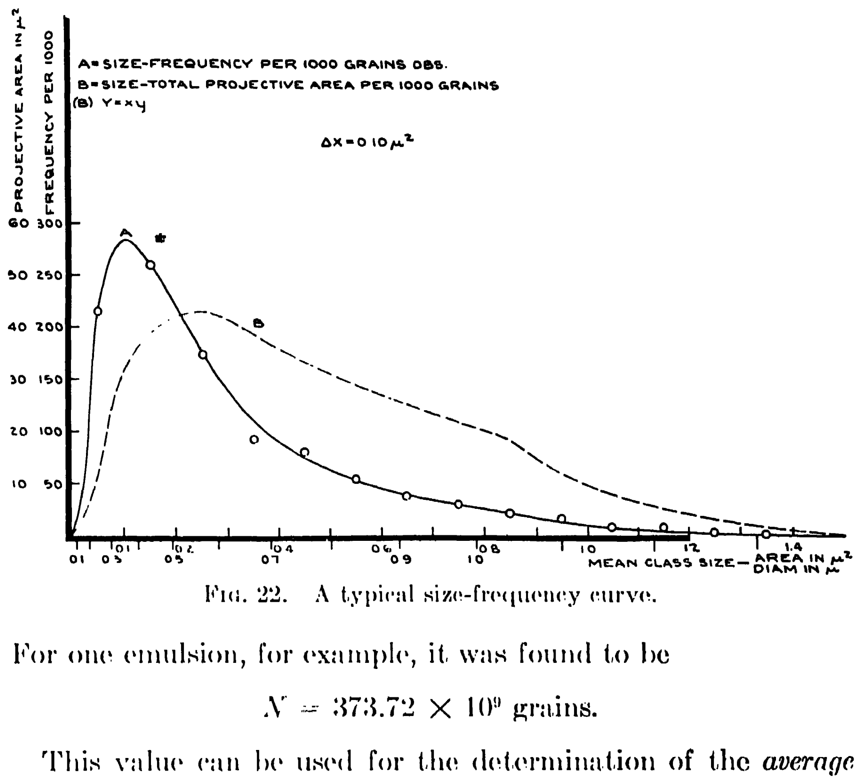

Fig. 22. A typical size-frequency curve.

For one emulsion, for example, it was found to be

$$N = 373.72 \times 10^9 \text{ grains.}$$

This value can be used for the determination of the *average thickness* of the grains and their total surface per cubic centimeter of emulsion.[17] Taking the specific weight of silver halide as 6.47, the volume of the silver halide per cubic centimeter of the emulsion is calculated from the known concentration of silver halide in the emulsion. It was found to be 5.7×10^{-3} cc. This volume, divided by the total projective area of the silver halide grains per cubic centimeter of emulsion ($N \times \bar{a}$), gives the average thickness (*th*) of the grains, which in this case is $11.1 \times 10^{-2}\mu$. If the projective area of a silver halide grain is an equilateral triangle, the ratio of length of side to average thickness is 4.8. The total surface (A) is found to be

for a triangle: 3.4 times the projective area
square: 3.3 " " "
circle: 3.1 " " "

The average of these values is 3.3, which is used to calculate the total surface of the silver halide grains per cubic centimeter of emulsion and gives 1693 square centimeters. There is some doubt whether this method is really entirely trustworthy. A combination of measurements of the projective area and counts of the number of particles does not lead to satisfactory results if used to determine the thickness of grains which appear to be cubical. Further experimental work on the subject is required.

Other characteristics of grains are the average volume and the average weight. These can easily be calculated from the other data.

The average grain sizes ($\bar{a}$), measured as the projective area in μ^2, the spread of grain-size distribution (σ), also in μ^2, and the total number of grains (N) per cubic centimeter of emulsion of a few commercial emulsions are given in the following table:

TABLE IV

Plate or Film	$\bar{a}$ *in* μ^2	σ *in* μ^2	$N \cdot 10$ [illegible]
Motion-picture positive film	0.31	0.25	117.85
Fine-grain roll film	0.49	0.58	52.35
Portrait film	0.61	0.75	25.66
High-speed roll film	0.93	0.81	22.61
X-ray film	2.30	1.03	6.32

The accuracy of the size-frequency determination increases as the square root of the number of grains measured, so that an increase in accuracy involves a considerable increase in the work of making the determination. The number of grains which must be measured increases with the dispersion, which, in turn, is approximately proportional to the average grain size. The number necessary depends somewhat on the regularity of the shape of the grains, but Trivelli concluded that, if the following numbers of grains are measured for the different values of $\bar{a}$ and σ, satisfactory accuracy will be attained.

$\bar{a}$	σ	n
0.12	0.10	400
0.18	0.17	500
0.36	0.35	600
0.54	0.48	700
1.18	1.14	800
1.91	1.69	900
2.82	2.40	1000

The sensitivity of the grains can be investigated in two ways: Svedberg gave one-grain layer plates a series of controlled exposures, developed the plates, and removed the developed grains in a diluted solution of chromic and sulfuric acids. He determined the grain-size distribution of the unexposed part and subtracted from this the grain-size distribution of the grains left in the exposed parts, which determined the grain distribution of the affected grains. It was found that in all the emulsions investigated, the larger grains were more sensitive than the smaller grains. The greatest errors in this method occur quantitatively in the regions of very short exposures. To avoid this, Silberstein and Trivelli[18] made use of the fact that some pure silver bromide emulsions if developed with hydroquinone give silver particles of the same size and shape as the original grains. This makes it possible to determine directly the size-frequency curve of the grains affected by different exposures. The method is limited to a special emulsion and a special developer and is not of such general applicability as Svedberg's.

The growth of the silver bromide grain during digestion was studied by Loveland and Trivelli[14a] in a series of emulsions measured at different stages. The size-frequency curves obtained, which were plotted on double-logarithmic paper, resemble parabolas, of which the foci lie on a straight line. In Figure 23*b*, the positions of the parabolas are shifted to show that the double-logged size-frequency distributions corresponding to different stages of digestion were unchanged in shape. The same was the case with the normal functions. The logarithms of the frequency characteristics, y, total number of grains, average grain size, and dispersion are directly proportional to the logarithms of the times of digestion, x; that is, they vary according to the simple exponential equation

$$y = Cx^b,$$

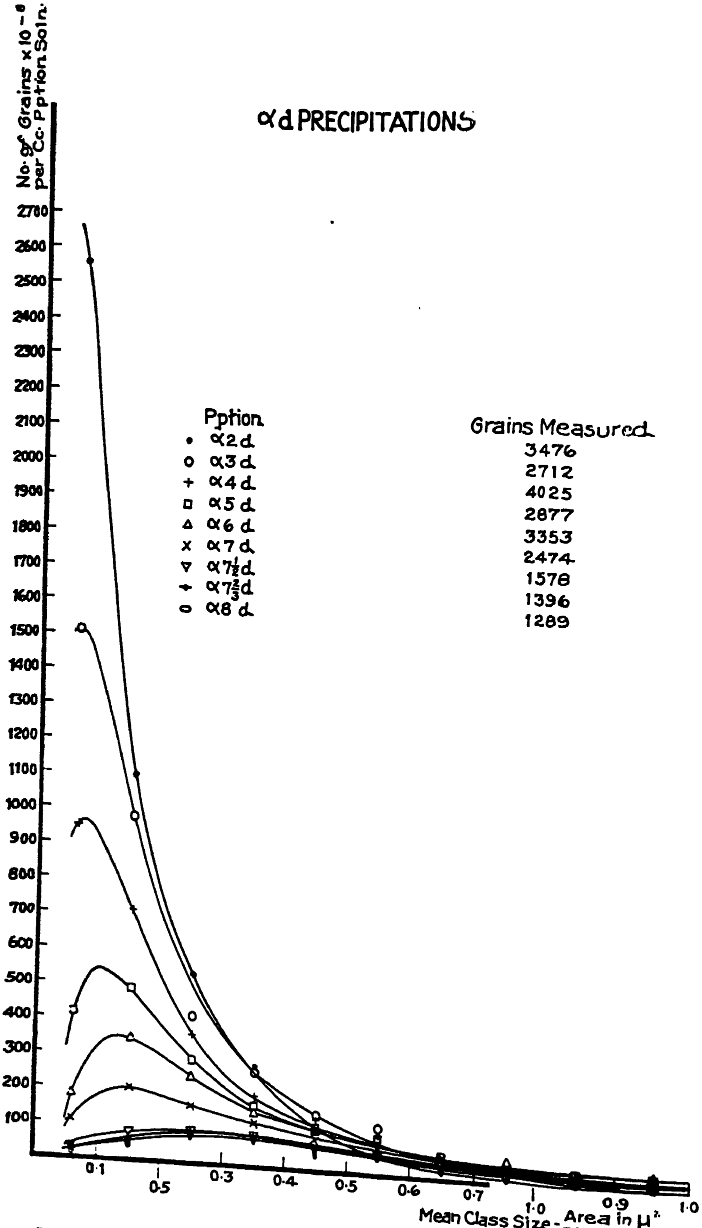

FIG. 23*a*. Size-frequency curves from a series of digestions.

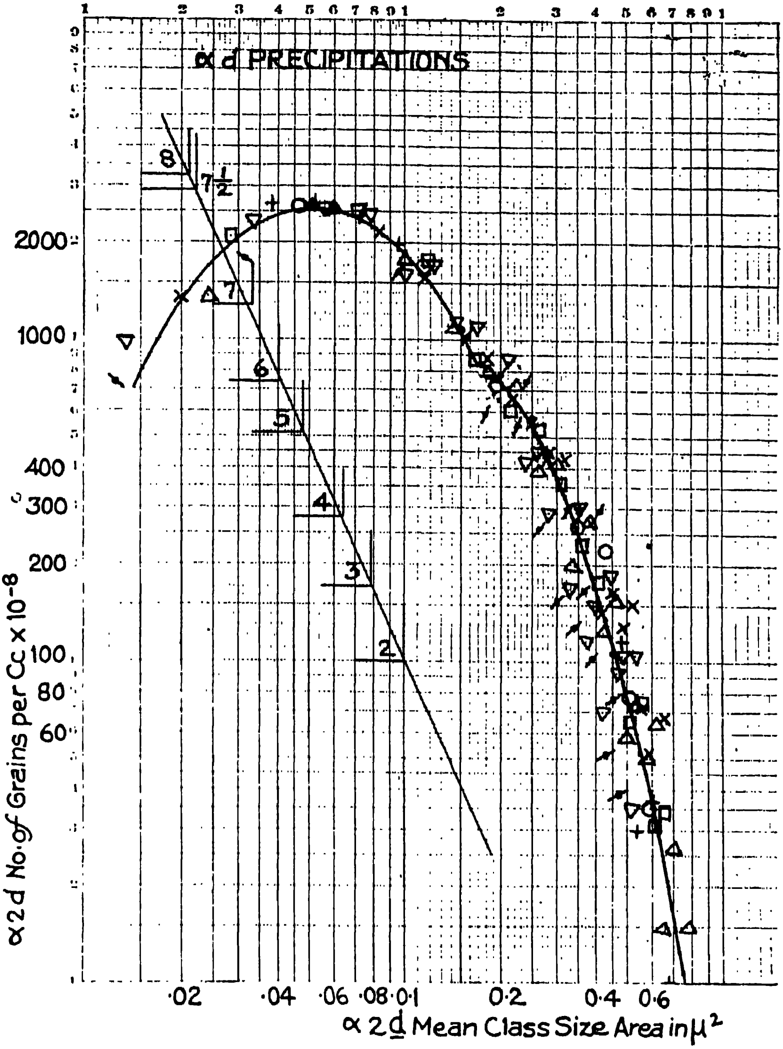

FIG. 23b. A curve plotted on double-logarithmic paper to show the identity of shape.

in which C and b are constants. The same type of equation was also found to hold for the grain growth during precipitation and ripening in an emulsion made by a different method. The average thickness of the grains increases rapidly at first to a certain value and then does not change appreciably during further precipitation and ripening within the emulsion-making range. Growth of these grains takes place mainly in two dimensions, which results in the formation of large tablets. Trivelli and Smith found in another series of emulsions with different silver iodide concentrations that the grains become smaller with increasing iodide content as far as their projective areas are concerned.

Trivelli and Smith[19] investigated size-frequency relations in several emulsion series in which the time of precipitation of the silver halide was varied. The same type of exponential relations as those described above was found between:

1. The average grain size and the dispersion of grain sizes, approaching in many cases a straight line.
2. The average grain size and the average thickness of the grains.
3. The total number of grains per cubic centimeter of the emulsion and the average grain size.
4. The total surface of the grains per cubic centimeter of emulsion and the average grain size.
5. The dispersion and the average thickness of the grains.
6. The dispersion and the total number of grains per cubic centimeter of emulsion.
7. The dispersion and the total surface of the grains per cubic centimeter of emulsion.

A straight-line relation was found for the average grain size and the time of precipitation.

The size-frequency characteristics can also be correlated with the sensitometric characteristics. There is the same type of exponential relation between the time of precipitation and the contrasts of the emulsions and between the average grain size and the contrast. The same relation holds also between the H and D speed and the average grain size. This relation is close to a direct proportionality in many cases. Trivelli and

Smith[20] found that γ is proportional to the square root of the number of grains per square centimeter of emulsion.

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CHAPTER III

THE PREPARATION AND PROPERTIES OF GELATIN

The medium in which the light-sensitive silver halide particles of a photographic emulsion are suspended must satisfy a number of exacting requirements. It must keep the emulsion grains perfectly dispersed to eliminate clumping and consequent granularity of the photographic image; it must be stable for a long period of time, so that both the undeveloped and the processed emulsion are reasonably permanent; it must impart no undesirable photographic characteristics to the emulsion grains; it must be such that it can be handled in a relatively simple and yet accurately reproducible manner, so that emulsions can be made and coated by practicable procedures; and, finally, it must allow the penetration of processing solutions without impairment to its strength, toughness, and permanence after the processing operations are completed.

Gelatin satisfies these requirements and, in addition, has certain chemical properties which are indispensable for the preparation of emulsions of high sensitivity. The earliest emulsions, which were made with collodion, lacked both the physical and chemical properties necessary for the best results. Extensive searches for emulsion media better than gelatin have as yet been unsuccessful.

In a discussion of the properties of gelatin, it is necessary to consider the physical and chemical properties which make it preeminent for use in photographic emulsions and to study briefly the essential chemical structure responsible for its physical behavior.

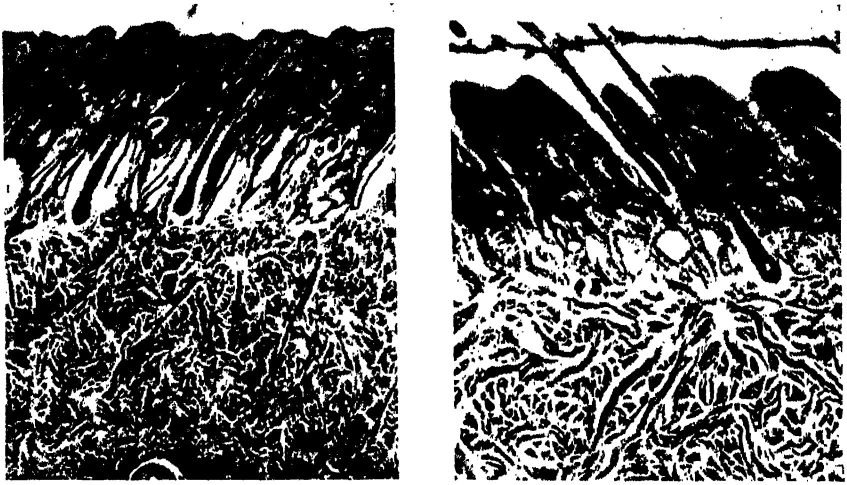
THE SOURCE AND PREPARATION OF GELATIN

Unlike the silver halides, the jelly constituent of an emulsion is not a sharply defined chemical individual. Gelatin is preeminently a substance with a history; its properties and its future behavior are intimately connected with its past. Gelatin is closely akin to glue. At the dawn of the Christian era, Pliny wrote, "Glue is cooked from the hides of bulls." It is described equally shortly by a present-day writer [1] as "the dried down soup or consommé of certain animal refuse." The process of glue-making is age-old and consists essentially of the boiling down of hide clippings of such animals as cattle, sheep, pigs, and rabbits, or the bones of the first three. The filtered soup is allowed to cool and set to a jelly which, when cut and dried on nets, yields sheets of glue or gelatin, according to the selection of stock and the process of manufacture. In the preparation of glue, extraction is continued until the ultimate yield is obtained from the material; in the case of gelatin, however, the extraction is halted earlier and is carried out at lower temperatures, so that certain strongly adhesive but nonjelling constituents of glue are not present in gelatin. Glue is thus distinguished by its adhesive properties; gelatin, by its cohesive properties, which favor the formation of strong jellies.

Photographic gelatin is generally made from selected clippings of calf hide and ears, as well as cheek pieces and pates. Pigskin is used for the preparation of some gelatins; and large quantities are made from bone, the bone being decalcified to form ossein.

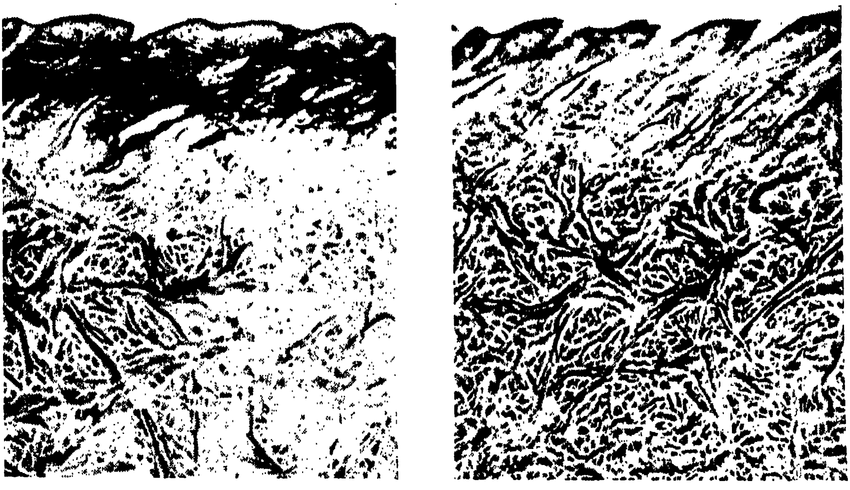
The raw materials are selected not only for good structural quality but for freedom from bacterial decomposition. A section through a typical piece of hide is shown in Figure 24. In preparation for the extraction, the dirt, with loose flesh and blood, is eliminated in a preliminary wash. The hair, fat, and much of the albuminous materials are removed by liming; in this operation, the stock is allowed to soak for about two months in limewater containing suspended lime. The free lime continues to rejuvenate the solution and keeps the bath at suitable alkalinity. This operation is followed by deliming with dilute acid, washing, and cooking to extract the gelatin. Several "cooks" are made at increasing temperatures, and usually the products of the last extractions are not employed for photographic gelatin. When the gelatin has been extracted, there is left a residue, which consists chiefly of elastin and reticulin with some keratin and albumin. The crude gelatin solution is filtered, concentrated if necessary, cooled until it sets, cut up, and dried in slices.

Gelatin may also be made by an acid treatment of the stock without the use of lime: The stock is treated with dilute acid (pH 4.0) for one to two months and then washed thoroughly and extracted. This gelatin differs in properties from gelatin made by treatment with lime.



Vertical section of calfskin from butt

Calfskin after liming for two days



Calfskin before deliming

Calfskin after deliming

FIG. 24. Photomicrographs of a section of cowhide. About ×20. (From *Viewing Leather through the Eyes of Science*, Dr. John Arthur Wilson, chief chemist, A. F. Gallun & Sons Co., Milwaukee, Wisconsin.)

THE CHEMICAL PROPERTIES OF GELATIN

The actual fleshy substance in the skin furnishing the gelatin is *collagen.* The corresponding connective tissue obtained from bone is termed *ossein.* The collagens are proteins, jelly-forming albuminoids, which contain little sulfur and disperse slowly in hot water. In passing into solution, they hydrolyze irreversibly into gelatin. Sheppard and Houck,[2] as the result of studies of the viscosities of gelatin solutions and in agreement with the X-ray diffraction investigations of Meyer and Mark,[3] suppose that collagen consists of fibers built up of long molecular chains. Hydrolysis results principally in the separation of the molecular chains owing to rupture of cross linkages accompanied by a less important decrease in the length of the dispersed chains. The resulting molecules pass into solution as gelatin.

Küntzel and Koepff [4] consider that in the formation of gelatin from collagen, the liming operation causes a partial breakdown of the peptide linkages and of some of the intermolecular valence forces in the fiber; this step is termed *topochemical hydrolysis* to distinguish it from hydrolysis leading to solubilization of the material in the form of gelatin.

The next step in the preparation of gelatin, the cooking operation, causes a further breakdown of cross linkages, followed by solution and the coiling up of the liberated long gelatin molecules which exist in an extended state in the natural fiber. Since the coiled state is thermodynamically more stable than the extended state, the molecules cannot take their original configuration, and gelatin formation is irreversible. Further hydrolysis results in the breakdown of the gelatin molecules into smaller molecular units, and the characteristic properties of the gelatin are lost. Evidence for the step involving the coiling of gelatin molecules is found in an investigation of Sheppard and Houck,[5] who showed that a partial reversal of the process of gelatin formation is effected when highly stretched gelatin gels are heated to insolubility. The insoluble material showed an X-ray diffraction pattern like that of collagen and had substantially all of the physical properties of collagen.

The forces which hold the gelatin molecules together in the form of collagen fibers may be of three types: strong covalent bonds, electrostatic bonds arising from the electrically polar groups in the molecules, and hydrogen bonds. It is possible that the topochemical hydrolysis of Küntzel and Koepff involves a partial fission of the covalent links, during which reaction the gelatin molecules are held together by electrostatic and hydrogen bonds. The formation of gelatin during the cooking operation would then presumably be due to the rupture of the remaining covalent links and the loosening of the weaker electrostatic and hydrogen bonds.

Astbury [6] concluded from X-ray diffraction studies that the breakdown of collagen to gelatin involves both a decrease in the length of the main molecular chains and in the average number of molecules in the chain bundles.

That the principal change involved in the formation of gelatin from collagen is the separation of individual molecules from the fibers is borne out by the analysis of the parent substance and its product. Thus, the compositions of collagen and ash-free gelatin are as follows:

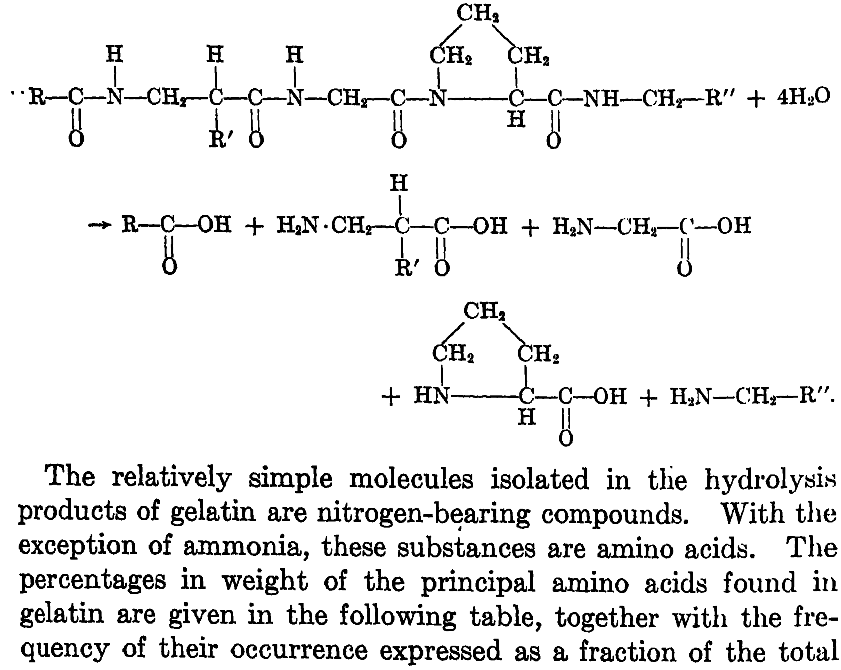
	Carbon	*Hydrogen*	*Nitrogen*	*Oxygen*
Collagen (Hofmeister[7])	50.7	6.5	17.9	24.9
Gelatin (Smith[8])	50.5	6.8	17.5	25.2

There are, however, definite chemical changes involved in the gelatin-forming process. Thus, although the acidic properties of an acid-processed gelatin are very like those of the original collagen, this is not true of lime-processed protein. These facts show that certain hydrolysis reactions have taken place which involve the gelatin molecule itself.

Gelatin derived from animal hides probably contains a small percentage of keratin, another protein, or of its degradation products. A more important constituent is albumin, which may be present up to about one per cent.[9] Both keratin and albumin contain small amounts of sulfur, which is of great importance in the production of emulsions of high sensitivity. This is discussed later. Gelatin also contains small amounts of carbohydrates, principally galactose and glucose.[10]

From chemical and physical data, including X-ray diffraction pictures, it has been established that the long gelatin molecules are made up of a number of regularly recurring groups or residues which, upon drastic hydrolysis, split into small discrete molecules which retain their identity. It is not possible to state absolutely that the ultimately segregated molecules are not degradation products of molecules of intermediate size, but the chemical and physical data strongly indicate that this is not the case.

The degradation of a simple polypeptide chain by hydrolysis can be illustrated as follows:



The relatively simple molecules isolated in the hydrolysis products of gelatin are nitrogen-bearing compounds. With the exception of ammonia, these substances are amino acids. The percentages in weight of the principal amino acids found in gelatin are given in the following table, together with the frequency of their occurrence expressed as a fraction of the total number of molecules:

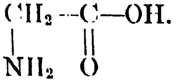
TABLE V

PERCENTAGES OF AMINO ACIDS IN LIME-PROCESSED GELATIN AND THEIR FREQUENCY OF OCCURRENCE

Amino Acid	*Percentage*	*Frequency*
Glycine	25.5	1/3
Alanine	8.7	1/9
Aspartic acid	3.4	
Glutamic acid	5.8	
Arginine[a]	6.2–7.8	1/18
Lysine	5.9	1/24
Histidine[a]	0.3–0.5	
Proline	19.4	1/6
Hydroxyproline	14.4	1/9
Leucine	7.1	1/18
Phenylalanine	1.2	
Serine	0.4	

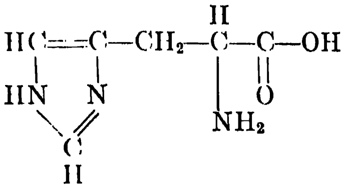
[a] Unpublished data of S. E. Sheppard and co-workers.

The amino acids contain —NH_2 and —COOH groups, the structure of the simplest of them, glycine, being

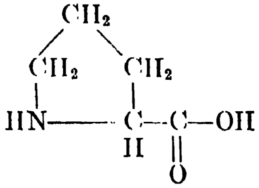


$$\underset{\displaystyle NH_2}{\underset{|}{CH_2}}-\underset{\displaystyle O}{\underset{\|}{C}}-OH.$$

They are derivatives of the fatty acid series. Some of the amino acids contain rings; *e.g.*, the structure of histidine is



and of proline is

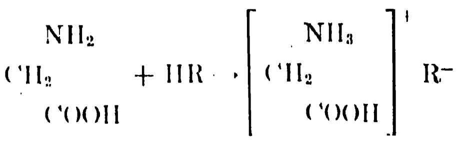


Since the amino acids contain both the acid carboxyl group and the basic amino group, they are amphoteric. If sodium hydroxide is present, the amino group is unaffected, but the carboxyl reacts to form a salt. In the presence of strong acid, the carboxyl group is inert, but the amino group adds the acid molecule and forms a salt. In general symbols, the two reactions for gelatin may be written:

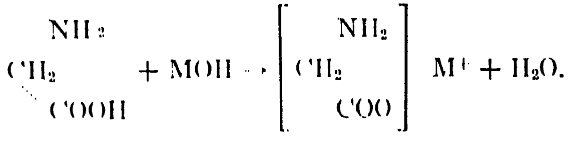
HR + gelatin → gelatin salt of R

MOH + gelatin → M gelatinate

For glycine, the reactions are:

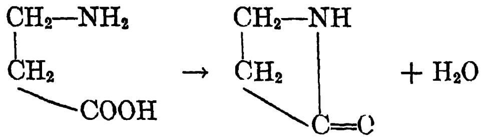


$$\begin{matrix}NH_2\\CH_2\\COOH\end{matrix} + HR \rightarrow \left[\begin{matrix}NH_3\\CH_2\\COOH\end{matrix}\right]^+ R^-$$

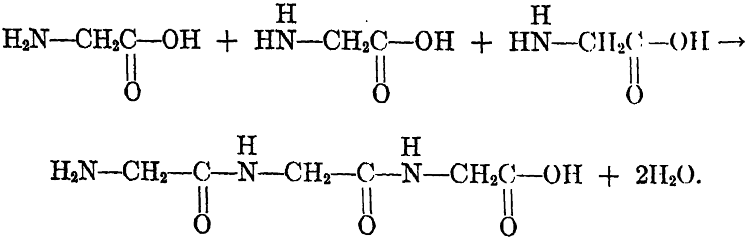


$$\begin{matrix}NH_2\\CH_2\\COOH\end{matrix} + MOH \rightarrow \left[\begin{matrix}NH_2\\CH_2\\COO\end{matrix}\right] M^+ + H_2O.$$

The acid and basic groups in a single amino-acid molecule can react with each other, or these active groups can react with such groups in other molecules. Thus, the intramolecular condensation



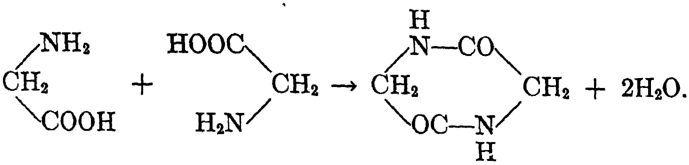
may occur. There are two types of intermolecular condensation possible for amino acids. The first of these results in the formation of straight-chain compounds and is presumably the reaction responsible for the building up of the giant protein molecule from the amino-acid units. Thus, in a simple case,



$$H_2N{-}CH_2\underset{\overset{\|}{O}}{C}{-}OH + H\overset{H}{N}{-}CH_2\underset{\overset{\|}{O}}{C}{-}OH + H\overset{H}{N}{-}CH_2\underset{\overset{\|}{O}}{C}{-}OH \rightarrow$$

$$H_2N{-}CH_2{-}\underset{\overset{\|}{O}}{C}{-}\overset{H}{N}{-}CH_2{-}\underset{\overset{\|}{O}}{C}{-}\overset{H}{N}{-}CH_2\underset{\overset{\|}{O}}{C}{-}OH + 2H_2O.$$

A second, less important intermolecular condensation which may occur to some extent in protein formation involves cyclization. An example of this type of reaction is the formation of diketopiperazine.



A number of polypeptides have been synthesized from amino acids, in one case as many as nineteen amino-acid units having been linked together. These synthetic materials closely resemble the proteins in many of their properties.

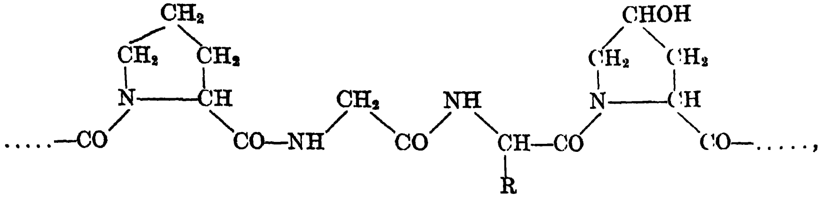
The manner in which the individual amino acids fit into the giant gelatin molecule has been determined with some degree of certainty. The chemical data on the degradation products of gelatin and the knowledge of the types of chemical reactions which amino acids can undergo provide restrictions which must be met by any proposed structure. The arrangement of the amino-acid units in the chain which makes up the gelatin molecule has been studied by means of X-ray diffraction measurements. The early work of Katz, Meyer, and Mark, and others has been amplified by other investigations; and most recently Astbury [6] has contributed greatly to knowledge of the structure of gelatin as derived from diffraction data.

X rays falling upon a substance are diffracted by its component atoms or groups, the intensity and direction of the diffracted rays being determined by the kinds of atoms or groups and their arrangement in the substance. If the inner structure of the substance is made up of regularly recurring and definitely oriented atoms or groups, the diffraction pattern of the X rays is well defined; lack of a definite pattern indicates the lack of a regular internal structure. From the spacings of a definite X-ray diffraction pattern, the arrangement and dimensions of the internal units can be calculated directly from well understood physical principles. The results of Astbury's analysis of the X-ray diffraction patterns of collagen and gelatin lead to the following structures: In collagen, the long individual molecular chains are held together in the form of a grid by cross linkages between the side chains. The average distance between chains varies with the humidity but is 10.4 A. for thoroughly dried collagen. The distance between adjacent grids is approximately 4.4 A. In the transition to gelatin the cross linkages are broken. The chains, somewhat hydrolysed, are made up of amino-acid residues whose average length along the molecular axis is 2.9 A. The best evidence indicates that the average chain is 838 A. long or a multiple thereof and is made up of 288 amino-acid units. The average molecular weight is about 27,000 or some multiple of this. To account for the short average amino-acid length along the direction of the chain, it is necessary to assume a zigzag structure.

The final choice as to the arrangement of the amino-acid residues along the chain of the gelatin molecule is governed by the frequencies given above in Table V. The high percentages of proline plus hydroxyproline and of glycine residues lead to the arrangement

. . . . . . —P—G—R—P—G—R—P—G—R— . . . . .,

where P stands for either proline or hydroxyproline, G for glycine, and R for one of the other amino-acid residues. This grouping repeats itself until the average molecular weight is 27,000 or a multiple of 27,000. In conventional symbols, the structure is written



where R is a side chain. The pattern of three amino-acid residues is not actually the true unit in the direction of the molecular axis, since there are minor variations in the arrangement. These arise in three ways: first, because the cyclic structure may be either proline or hydroxyproline; second, because once in every eighteen residues the ring is missing; and, third, because the side chain R is variable. These variations are of minor importance, however, in determining the arrangement of the grid-like structure of collagen.

The Acid-Base Properties of Gelatin

Because of its amphoteric character, gelatin can act as either a base or an acid. Since both the basic and acid groups are weak, it exhibits the properties of a buffer, characterized by the fact that large additions of acid or alkali do not markedly affect the concentration of hydrogen ions. The buffer action of a gelatin solution depends upon its pH range and is determined by the acid and basic dissociation constants of the —NH_2 and —COOH groups present. Thus, the addition of constant quantities of acid or base to a solution does not produce constant changes in hydrogen-ion concentration. This is illustrated in Figure 25, redrawn from the data given by Cohn.[11]

The addition of progressive amounts of acid to a solution of a lime-processed gelatin causes a slow drop in pH to about 2.5.

This effect can easily be understood from the very small constants of dissociation of both the amino and the carboxyl groups. At a pH less than 7, the acid groups are somewhat dissociated, but the concentration of hydroxyl ions is still large enough between pH = 7 and pH = 2.5 to prevent the dissociation of the amino groups. The addition of acid in this region is used for neutralization of the amino groups.

From titration curves such as that illustrated, it is possible to derive acid and basic dissociation constants which can be ascribed to the various amino-acid units which constitute the gelatin molecule. The shapes of such curves depend on the process used in the manufacture of the gelatin, *e.g.*, lime-processed or acid-processed, and afford an indication of the chemical changes occurring during the transition from collagen to gelatin.

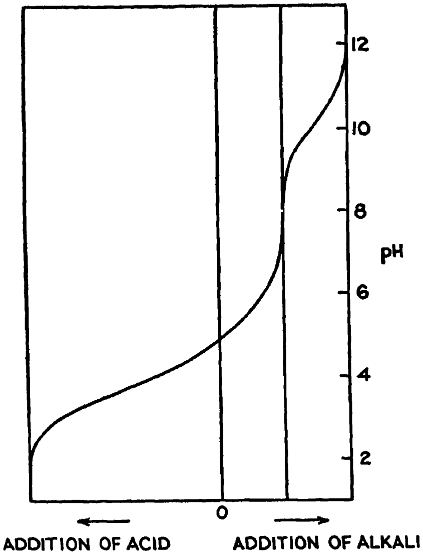


Fig. 25. The titration of gelatin with acid and alkali.

The Combining Power of Gelatin for Silver Ions

A chemical property of gelatin of interest primarily to the photographic chemist is the ability of the protein to enter into combination with silver ions. This property was studied by Carroll and Hubbard,[12] who found it has a marked dependence upon pH. The silver-ion combining power of gelatin decreases with decreasing pH but is still appreciable below a pH of 4. This is illustrated in Figure 26 from Carroll and Hubbard, in which the mols of silver ion combined per gram of gelatin at constant silver-ion concentration are plotted against pH for four values of [Ag^+]. The combination of silver ions with gelatin is probably due to the formation of complexes involving the basic amino groups of the gelatin molecule; this is supported by the fact that at low pH, where the $—NH_2$ groups are tied up with hydrogen ions, the affinity of the gelatin for silver ions is considerably reduced.

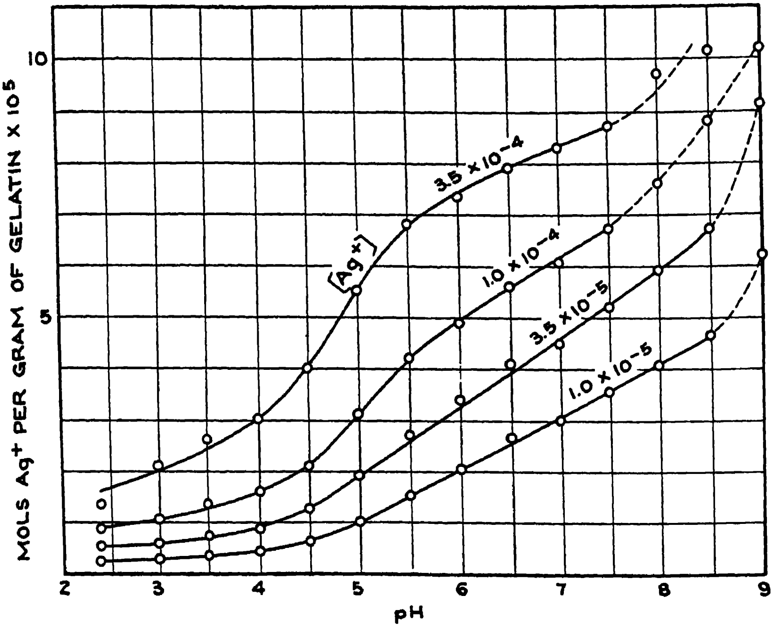


FIG. 26. The combination of silver with gelatin in relation to pH.

THE PHYSICAL PROPERTIES OF GELATIN

Dry gelatin stored under usual conditions, at humidities between 40 per cent and 70 per cent, contains about 10 per cent of moisture. It is tough and horny and has great mechanical strength but becomes harder and brittle when thoroughly dried. Placed in cold water, gelatin takes up liquid and swells to many times its original bulk, with little of the protein passing into solution. The swollen gelatin is flexible, soft, and easily torn; if the temperature is raised to about 40° C., it melts to a viscous liquid, or gelatin "solution," which may be diluted indefinitely. Provided the concentration is greater than one per cent, the solution sets to a jelly after standing for some time in a cool place. The strength and rigidity of the jelly depend upon the concentration of the gelatin. The properties of setting, melting, and swelling, among others, are discussed in more detail.

Isoelectric Point

Most of the physical properties of gelatin solutions are dependent upon the acidity or alkalinity of the solutions, and this dependence is intimately associated with the isoelectric point.

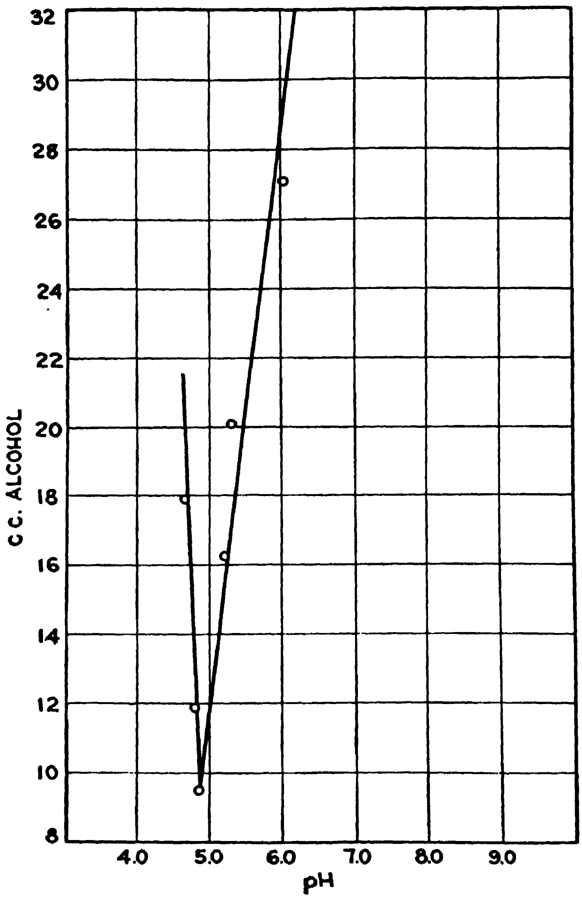


FIG. 27. Curve showing the amount of alcohol required to precipitate gelatin at various values of pH.

The isoelectric point of a substance is the pH value at which the material is electrically neutral, so that under the influence of an electrostatic field it migrates neither to the positive nor to the negative pole. The isoelectric point of an amphoteric substance such as gelatin is the pH at which it is equally dissociated as an acid and as a base, and it is also the point of minimum dissociation.[13]

In Figure 25, illustrating the acid-base properties of a lime-processed gelatin washed to complete removal of inorganic ions, the pH of the solution before the addition of acid or base is 4.8. This is the isoelectric point of the particular gelatin studied. Gelatins prepared by different procedures, *e.g.*, by acid or basic processes, have different isoelectric points, depending upon the hydrolysis reactions taking place during the manufacture. Thus, the isoelectric points of lime-processed gelatins may vary from 4.7 to 5.3, determined by the numbers and types of acid-amide groups destroyed and converted into ammonia. The isoelectric points of acid-processed gelatins, on the other hand, are nearer those of collagen and vary from about pH 7 to pH 9; these high values are due to the fact that few of the basic nitrogen groups are destroyed during the acid treatment.

Many of the physical properties of gelatin have their minimum values at the isoelectric point: *e.g.*, the solubility, the osmotic pressure, the degree of swelling, and the alcohol precipitation number. The alcohol precipitation number is a measure of the amount of alcohol required to bring about the first perceptible precipitation of the dissolved gelatin. Figure 27, taken from Sheppard and Houck, shows the effect of pH on the alcohol precipitation of gelatin. The isoelectric point determined by this method is 4.9. This value agrees well with that obtained by two other methods of measurement—light scattering and migration under the influence of an electric field.

Viscosity

Viscosity is one of the most important of the physical properties of gelatin. Viscosity is defined as the resistance opposed by a liquid to shearing force and is a measure of the resistance to flow of one molecule (or molecular aggregate) past another. The unit of viscosity is the *poise,* defined as one dyne per square centimeter per unit velocity gradient. The *centipoise,* $\frac{1}{100}$ of a poise, is used as the practical unit. A common method of measurement is to pass the liquid under a known head through a narrow capillary tube; the viscosity is expressed as the volume of solution passed per unit time divided by the force required to make it pass. For most liquids, the rate of shear is proportional to the shearing force; but for some a certain minimum force must be applied before any flow takes place. For greater forces, the rate of shear is related to the force in the normal manner. Such pasty liquids are said to possess plasticity. At low rates of shear, gelatin solutions have abnormally high viscosities; this indicates properties intermediate between viscosity and plasticity.

The viscosities of gelatin solutions do not remain constant with time and are dependent upon temperature, pH, source of gelatin, and other factors. The effects of some of these variables have been studied by a number of workers and discussed by Sheppard and Houck.[14]

Of two solutions made up at different temperatures, that at the lower temperature shows the greater rate of decrease of viscosity with time; but both rapidly approach the same rate of fall. Since, in gelatin solutions, hydrolysis is constantly occurring, it is desirable to reduce to a minimum the time required to bring the gelatin solution to a specified temperature of measurement.

The viscosities of gelatin solutions are strongly dependent upon pH, the shape of the pH-viscosity curves being determined to a considerable extent by the age of the solutions. This is illustrated in Figure 28, which shows a break or minimum in the curves at the isoelectric point. Attempts to correlate the viscosities of gelatin solutions with their concentrations have not been successful. The effect of temperature is complex. At relatively low temperatures, the viscosity rises with time; at somewhat higher temperatures, the viscosity first rises, then falls; at still higher temperatures, the viscosity shows a steady drop. There is no temperature at which the viscosity remains constant.

Sheppard and Houck think that the behavior of the viscosities of gelatin solutions is due to the coexistence of two opposing factors *gelation* (or jelly formation) and hydrolysis. Gelation causes an increase in viscosity, due to the setting up of a highly oriented structure in which the molecules are no longer free to move individually; and hydrolysis brings about a decrease in viscosity, owing to a lowering of the average molecular weight.

At low temperatures, gelation outweighs hydrolysis; and at high temperatures, hydrolysis is more rapid than gelation. At intermediate temperatures, gelation comes rapidly to a state approaching equilibrium, while the hydrolysis continues at a more or less constant rate and soon overcomes the initial increase in viscosity. From their studies, Sheppard and Houck conclude, in agreement with deductions made by Simms [15] from a study of the ionic activity of gelatin, that gelatin solutions contain molecularly dispersed, long-chain molecules. The viscosity effects of such a system are probably due to the formation of hydrogen bonds and to other types of intermolecular orienting forces. Solvation is apparently not a factor.

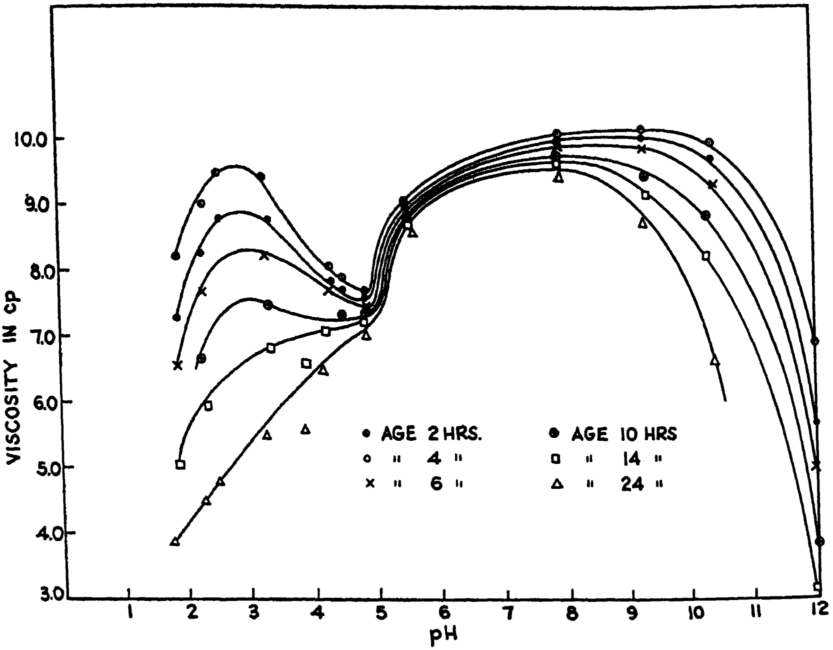


FIG. 28. Curves showing the relation between the viscosity of gelatin solutions and their pH value.

Setting and Melting

If allowed to stand at low temperatures, a gelatin solution solidifies; with an increase of temperature, it melts. The setting and melting points do not ordinarily coincide; and they are dependent not only on the concentration but on the pH, the neutral-salt content, the past history of the sample, and other factors. Furthermore, the points are ill defined. Just before setting, the solution becomes viscous to the point of stiffness; while immediately before melting, the jelly loses its mechanical strength. The particular moment in the softening process which is called *melting* has to be chosen arbitrarily. C. R. Smith takes the point when a bubble ½ cm. in diameter imprisoned in the mass just begins to rise; Küttner and Ulrich, when the jelly surface in a horizontal test tube just begins to sag. Sheppard, regarding the increase in viscosity through plasticity as a continuous change, prefers to define the melting point dynamically as the region of greatest alteration of property, or the point at which the elastic modulus becomes negligible.

The differences between the setting and the melting points of gelatin solutions are illustrated in Figure 29.[16] The region enclosed between the curves is one of imperfect thermal equilibrium. Above the upper curve, the solutions show little plasticity and behave as viscous liquids; the region below the lower curve is one of elastic gels.

There has been much speculation about the structure of gelatin sols and gels. Some of this is of interest from an historical standpoint. C. R. Smith deduced from polariscopic studies that gelatin solutions contain two species, sol and gel forms; the interpretation of his data has been questioned, and at present his views are not accepted. R. H. Bogue considered that gelatin solutions contain molecular chains which polymerize and link together to form a solid network when jelly formation occurs; his picture is somewhat vague, but if the term *polymerization* is broadly interpreted, it is not incompatible with present views. Procter and Katz pictured the gel state as a true solid solution which passes into a two-phase emulsion on melting, while Wo. Ostwald held the opposite view in postulating that jellies are composed of deformed liquid globules within a liquid phase. Nägeli proposed a micelle theory for the structure of gelatin sols and gels, which has been developed by McBain. The micelle is an aggregate in which each molecule retains its chemical individuality while losing its physical freedom. Thus, the chemical properties are those of the individual molecules, but the physical properties are governed by the behavior of the aggregates.

The various theories of the structure of gelatin sols and gels just described appear now to be incorrect. Evidence recently adduced can best be explained on the assumption that the micelles in gelatin solutions above a certain temperature are either the individual long-chain molecules of the polypeptide or accidental knots or tangles of such molecules.[17] X-ray diffraction pictures of gelatin sols and gels show that in the gel state the molecules are definitely oriented in a crystalline pattern. Above the melting temperature, however, the sol or solution shows no definite internal structure.[18]

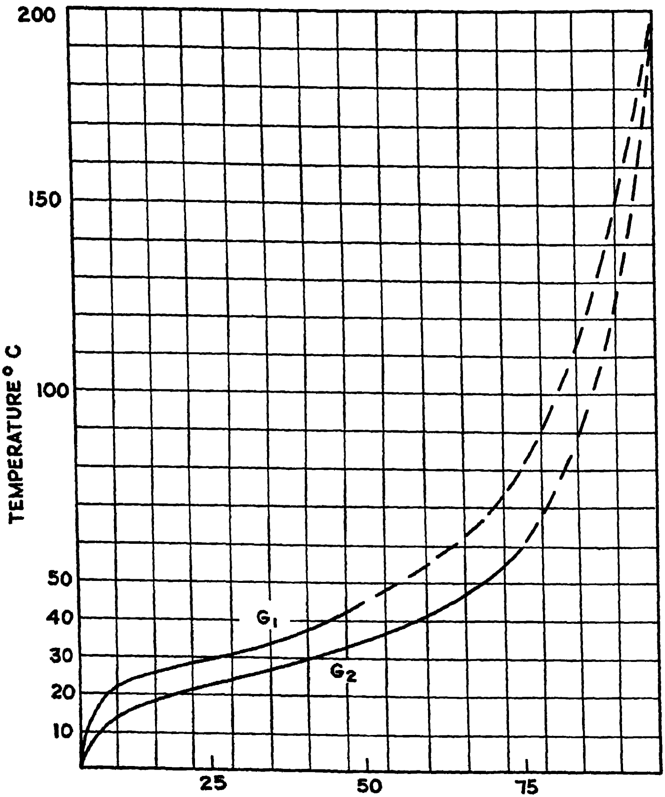


Fig. 29. The setting and melting points of gelatin solutions.

Gelatin sols, therefore, appear to be true solutions of large molecules; and setting to a jelly occurs if these scattered molecules come together to form a structural meshwork. The orientation of the molecules may be brought about by the formation of electrostatic cross linkages between the polar groups and also by the formation of hydrogen bonds between the —NH— and —CO— groups of adjacent molecules.[19] Hydrogen bonds are not true chemical bonds but are attractive forces resulting from resonance effects. Since the energy required to break a single hydrogen bond is only about 6 Calories, melting, or disorientation, can take place at low temperatures. Also, since the concentration of gelatin in solution determines the degree of proximity of one molecule to another, the higher the concentration, the greater the number of hydrogen bonds formed, and the higher the temperature necessary to break down the cross linkages.

Swelling

Dry gelatin absorbs water from a humid atmosphere or from the liquid. During this process, the gelatin swells until it has absorbed a definite amount of water, the equilibrium state being determined by temperature and other factors. During swelling, considerable pressure is developed until equilibrium is reached, when the pressure drops to zero.

The absorption of water vapor by gelatin has been investigated by Katz [20] and by Sheppard, Houck, and Dittmar.[17] In the experiments, gelatin sols of fixed concentration were prepared, coated on a support, and thoroughly dried at room temperature. The moisture absorption or regain at equilibrium was then measured under a variety of conditions. As for most cases in which colloidal materials are studied, the conclusions drawn apply to the specific conditions employed.

The moisture absorbed by dried gelatin is a function of the relative humidity of the environment and can be progressively removed by placing the material in an atmosphere of lower relative humidity than that with which it is in equilibrium. This is shown in Figure 30 for de-ashed gelatin at a pH of 6 at 25° C. The shapes of the absorption and desorption curves are the same, but the curves do not coincide. Such hysteresis effects are common in colloidal systems.

The moisture taken up at a fixed relative humidity depends upon the pH to which the original sol was adjusted before drying. It rises rapidly with the pH of the sol from pH 2 to pH 5, then levels off at values above this; there is no discontinuity in the curve at the isoelectric point of the gelatin, such as found for absorption from liquid water. The moisture regain decreases with increasing concentration of the original sol, dropping rather sharply for samples made up from sols of concentration greater than 10 per cent. Hydrolysis of the original gelatin over a range which reduces the viscosity by a factor of three has little effect on the absorption properties. Hardening gelatin by means of chrome alum and formaldehyde does not appreciably affect its absorption properties.

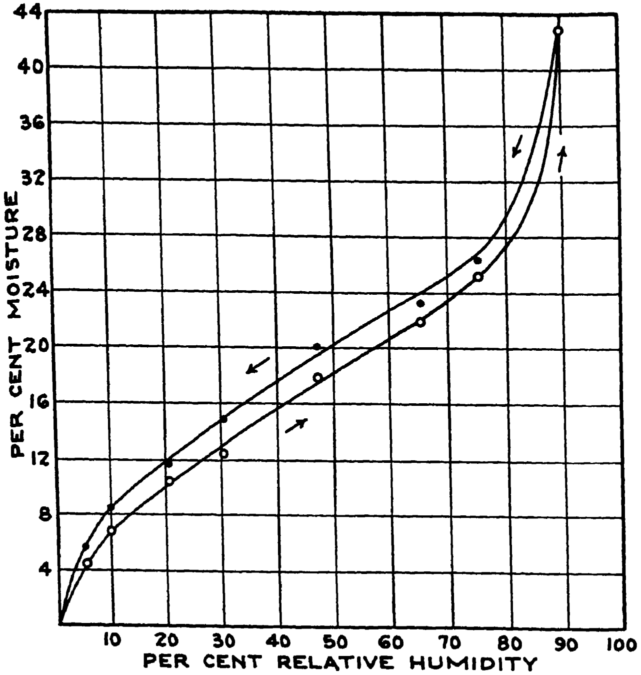


FIG. 30. Relation between the moisture absorbed by dried gelatin and the relative humidity. Adsorption, ○; desorption, ●.

Two types of gelatin were studied by Sheppard, Houck, and Dittmar. A lime-processed calfskin gelatin with isoelectric point at pH 4.8 and an acid-processed pigskin gelatin with isoelectric point at pH 8.2 showed very similar moisture absorption properties. No difference was found until humidities in the range of 80 to 90 per cent were reached, when the lime-processed material began to absorb much more water than the pigskin gelatin. This difference is much less than that found for the absorption of liquid water by such gelatins. Sheppard, Houck, and Dittmar conclude from their studies that there are two main forces influencing the absorption of water vapor; first, initial absorption at inner surfaces due to amino groups and, second, a continuation of absorption by condensation of water vapor in holes within the structure. From considerations of X-ray diffraction data, it appears that water is taken up within the crystallite gelatin structure between the principal valency chains, which extends the side-chain spacing.

The swelling by liquid water has been extensively studied. F. Hofmeister, in 1888–1891, investigated the effect of a number of substances on the swelling of gelatin and arranged the order of their increasing effectiveness as follows:[21] sulfates, citrates, tartrates, acetates, alcohol, cane sugar, dextrose, distilled water, chlorides, chlorates, nitrates, bromides, acids, and alkalis. For cations, the order was found to be: lithium, sodium, potassium, ammonium. The salts have a marked effect on the rigidity of the jelly and, in some cases, *e.g.*, thiocyanates and iodides, bring about an actual solution of the gel.

As a result of these observations and other facts, Loeb offered an explanation of gelatin swelling based upon Procter's application of the Donnan membrane equilibrium. The jelly is assumed to be made up of a number of cavities, the walls of which act as semipermeable membranes. These cavities contain substances, generally salts, which are responsible for the exertion of an osmotic pressure which causes the swelling. Donnan showed that if two solutions are separated by a membrane permeable to all the ions except one, an electrical potential and osmotic pressure are set up at the membrane surface between the solutions. Swollen gelatin is permeable to salt ions in aqueous solutions; and the walls of the pockets, singly or in series, constitute a membrane between the interior of the jelly and the outer liquid. The contents of the jelly form one solution, and the outer liquid, the other.

The swelling of gelatin in a dilute solution of hydrochloric acid serves as an example of membrane behavior. In the solution surrounding the jelly, there are hydrogen chloride, hydrogen ions, and chloride ions; in the gelatin, there is in addition to these substances, gelatin hydrochloride, which is partially dissociated. All of the species in the system are free to migrate except the gelatin ions, which are held in position because of intermolecular forces. These hold in their neighborhood an equivalent of chloride ions. The condition is illustrated diagrammatically as follows:

In the gel phase	*In the solution*
Gelatin	
Gelatin hydrochloride	HCl
Gelatin ions	H^+
Cl^- (Gel)	Cl^-
HCl	
H^+	
Cl^- (HCl)	

Since there is nothing to prevent the concentration of un-ionized hydrochloric acid being equal on either side of the membrane, the products of the hydrogen and chloride ions are also equal, from mass action concepts, since $\frac{(H^+)(Cl^-)}{(HCl)} = K$. On the jelly side, the chloride ions outnumber the hydrogen ions; hence, the total concentration of ions is greater in the gelatin than it is in the solution. The jelly, therefore, absorbs water, to compensate for its greater salt content, until the distending force is balanced by the tension of the fibrous structure

The swelling of gelatin in aqueous solutions is markedly affected by pH and is a minimum at the isoelectric point of the gelatin.[22] This is illustrated in Figure 31. This minimum swelling at the isoelectric point is in agreement with predictions of the Donnan theory, but the theory does not account for the fact that swelling occurs at all at the isoelectric point.

Northrup and Kunitz [23] attempted to reconcile gelatin swelling at the isoelectric point with the Donnan equilibrium theory. They postulate that gelatin sols contain an insoluble material which forms the membranes or walls of a number of particles or micelles and that each particle contains an internal liquid phase of soluble gelatin in water. The individual particles obey the thermodynamic requirements of the Donnan equilibrium and swell if placed in water. The authors found that gelatin can be fractionated into soluble and insoluble portions.

The theory of Northrup and Kunitz lacks independent experimental support and is vitiated by the experiments of Sheppard, Hudson, and Houck,[9] who showed that the insoluble fraction of

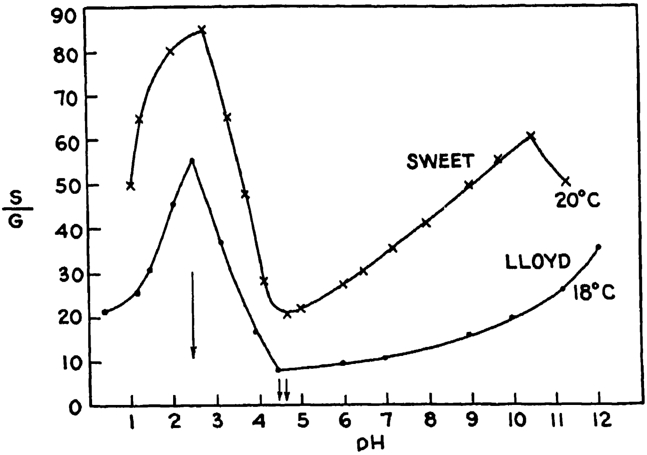


Fig. 31. Curves showing the swelling of gelatin in water in relation to pH. The swelling $\frac{S}{G}$ is expressed as the grams of water held per gram of gelatin.

gelatin is albumin and that its presence or absence did not affect the swelling. In addition, it was found that broken down, soluble material in a gelatin does not increase but actually diminishes the swelling until it is removed by diffusion; after this, swelling increases.

No generally satisfactory theory has yet been adduced to explain the swelling of gelatin at the isoelectric point. It seems probable that any explanation of the phenomenon must be based on the assumption that a gelatin jelly has a definite internal structure.

As is the case with vapor absorption, gelatin jellies made up at different concentrations before drying swell, if placed in cold water, to a limit which is determined by the original concentration of the jelly. For example, the gelatin dried from a 5 per cent jelly swells to a much greater extent than the gelatin dried from a 20 per cent jelly. If a piece of gelatin is put in water of moderate temperature, for example, about 15° C., the gelatin swells to a limited extent. If the temperature is raised much above this point, the gelatin continues to swell without limit and ultimately takes up all the water offered it; and the jelly breaks up into very small pieces. If, at this higher temperature, however, the water is replaced by a salt solution, the swelling is again limited.

Swelling is obviously complicated by many factors. One of these is the influence of the thickness of the dried gelatin layer. Swelling denotes an increase in volume due to the absorption of water. A layer of gelatin adhering to a photographic support can swell to a marked degree only in a direction perpendicular to the surface of the support; otherwise, the layer would have no definite dimensions and would not remain attached to the base. If gelatin is dried down on glass sheets so prepared that the dried gelatin can be stripped off, it is found, on placing the stripped sheets in water, that the greatest expansion still occurs in the direction perpendicular to the surface. There is, however, a considerable sidewise or lateral expansion on swelling, which shows that, if the sheet is attached to a rigid base, such as glass or film support, a force is exerted which tends to move the gelatin relative to the support. The amount of this force is proportional to the total swelling of the gelatin.

The absorption of water and the process of swelling must be regarded as impressing a strain on the gelatin. Gelatin and gelatin jellies have, in addition to bulk elasticity, the property of rigidity or elasticity of shape. If a material is stressed, it is desirable to keep the stress below the elastic limit if permanent deformations are not to be produced. In the case of gelatin, this means that undue swelling must be avoided. The type of swelling termed *unlimited swelling* indicates that the gelatin jelly has been strained beyond the elastic limit and is subject to permanent deformation. Factors tending to produce this condition are high acidity, high alkalinity, and high temperature.

Drying

The reverse of the process of swelling is the removal of water, or drying. Just as swelling imposes a strain on the gelatin, so also does drying. Drying involves two principal phases: (*a*) the diffusion of water to the surface of the jelly and (*b*) the evaporation of water from the surface. If process (*b*) is much more rapid than (*a*), that is, if diffusion cannot supply water to the surface as fast as it is removed by evaporation, strains involving persistent deformation are set up. This generally happens to some degree when gelatin materials are dried, because of the necessity for rapid drying.

The factors involved in the rapid drying of gelatin can readily be observed if freely suspended cubes of gelatin jelly are dried in an atmosphere of low relative humidity. The water is first removed from the corners and edges; this corresponds to the fact that, in photographic plates and films, drying starts from the edges. With continued drying of the cubes, a peculiar shape is developed, which indicates that very great strains are set up in the drying (Figure 32). These strains can be observed directly with a polariscope. In gelatin layers drying on supports, such as glass or film, the strains are held in check at the interface between the support and the gelatin or emulsion. With increased drying as opposed to swelling, however, the gelatin becomes more and more rigid and resistant to stress.

The forces operating at the interface during drying may be visualized in another way: The swelling of photographic emulsions is confined to the direction perpendicular to the support. Similarly, on drying, the contraction is confined to this direction. Since drying does not take place exactly reversibly to swelling, a new strain is produced in the material. Gelatin sheets subjected to swelling undergo some lateral as well as perpendicular expansion. The contraction of area during the drying of free swollen gelatin sheets cannot readily be measured, because the material curls and cockles. The contracting tendency can, however, be measured in the following way: If the gelatin is coated on supports of known rigidity and thickness and dried, the degree to which the rigid support is bowed is a measure of the contractility of the gelatin. This lateral contraction of the gelatin is the chief cause of its tendency when dry to strip from the support. If, on the other hand, the adhesion between the gelatin and the support is very strong, drying and the resultant contraction can exert a tremendous force upon the support, which may break or shatter under the strain. Thus, it is possible to shatter glass or extract slivers from its surface during the drying operation.

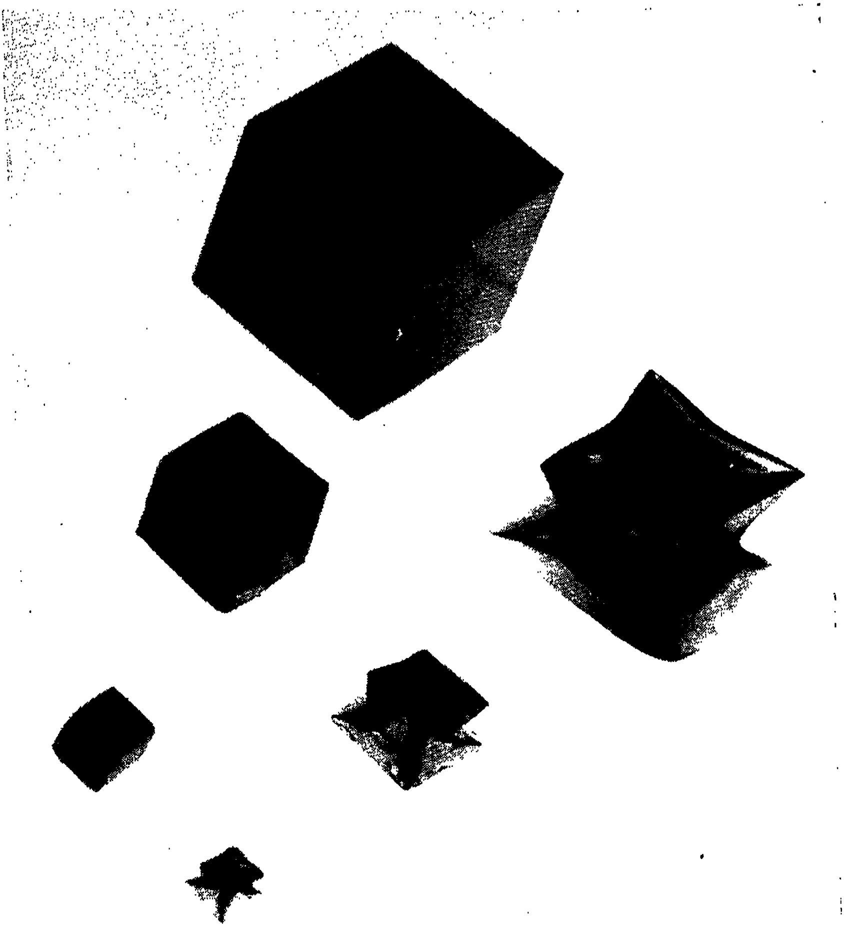


FIG. 32. Undried and dried gelatin cubes.

When a photographic emulsion is processed, it passes through a series of solutions which vary greatly in acidity and alkalinity; and changes are produced in the swelling of the gelatin which are of considerable importance in practice. The alkalinity of developing solutions would induce great swelling if it were not for the salts present. After development, the film is rinsed, the salts are diluted, and swelling is increased. Then the film is transferred to a fixing bath, which is usually acid. Here, a great strain in the gelatin structure is produced, which can be mitigated by the use of hardening agents. After fixation, the film is washed again, and swelling increases unless the film has been thoroughly hardened. Swelling increases rapidly with temperature and renders development processes difficult in tropical countries. The rate of washing of processed film is a function of the pH of the wash water, and the washing time is greater at the isoelectric point pH 4.7 than at pH 7.8 or pH 4.1. The time of drying, however, is a minimum for film washed with water at pH 4.7; this is due to the fact that less water is taken up during washing at this pH.

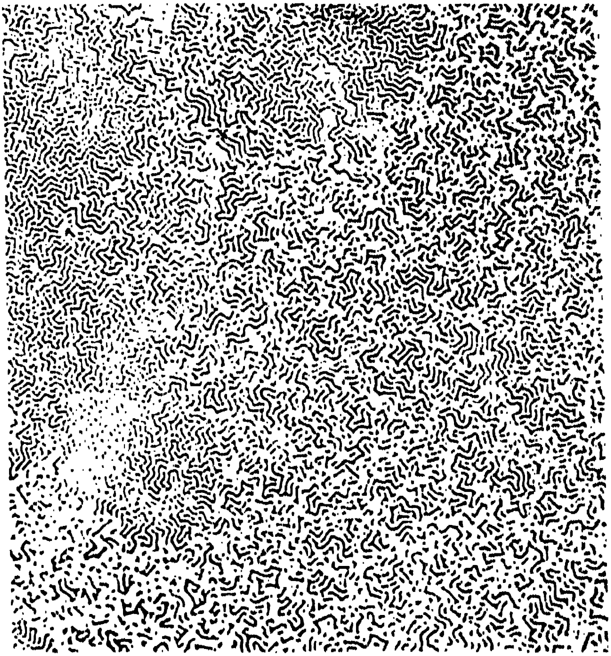


FIG. 33. Enlargement showing reticulation on an emulsion film after processing.

Reticulation is a condition produced by swelling and deswelling of the gelatin operating simultaneously but not at the same points (Figure 33). It can be brought about by simultaneous or successive treatment of the gelatin with swelling and dehydrating reagents.[24] A very common cause of reticulation is the use of wash water much warmer than the processing baths.

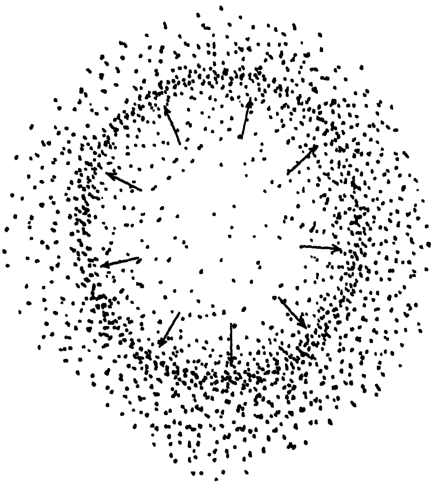


FIG. 34. Diagram of the migration of silver particles in a water spot.

Reticulation not only involves the production of mechanical relief but a movement of the particles of the image; these tend to aggregate in the ridges of the pattern, or grain, and to become fewer in the intervening valleys. This is an actual migration of silver particles owing to tension, similar to that occurring during the drying of moisture spots; the silver particles aggregate in the drying edge (Figure 34). An observation by Freundlich perhaps throws further light upon this effect. He found that suspended particles moving in an electric field migrate through gelatin jellies almost as easily as through water. This shows that within the jelly, under certain conditions, there is a high degree of mobility of solid particles coated with gelatin. This aspect of reticulation is probably a factor in producing graininess in the photographic image.

THE PROPERTIES OF GELATIN IN RELATION TO ITS USE IN EMULSION-MAKING

The gelatin used in a photographic emulsion is by no means an inert carrier of the silver halide grains. It behaves very differently from nitrocellulose, for instance, in which it is possible to suspend precipitated silver bromide but which has much less effect upon the silver bromide than gelatin.

The gelatin has several functions:

1. It acts as a protective colloid to maintain the dispersion of the silver halides and to protect them from reduction by a

developer without exposure. Although this action is commonly described as that of a "protective colloid," it can be produced by non-colloids, and is due probably chiefly to surface reactions.

2. In solution, it enables a stable suspension of silver halide particles to be formed.
3. In the jelly state, it supports mechanically the microscopic particles of silver halide and silver and permits soluble materials to act upon them.
4. It affects the sensitivity of the silver halide.
5. It combines with, and thus removes, the halogen liberated by the action of light.

The effect of gelatin on the dispersion of the silver halides is similar to that shown by many dyes, as pointed out by Lüppo-Cramer and others. A striking example is given by cyanine sensitizers. If a silver bromide sol (negatively charged) is titrated with very dilute dye solution, a point is reached at which all the silver halide is precipitated, all the dye added so far being carried down with it. If the titration is continued, the silver halide-dye precipitate commences to redisperse and can ultimately be entirely repeptized.[25] The dye does not act as a colloid; it is adsorbed irreversibly, exposing the portion of the molecules which has no affinity for water, and, when the whole silver halide surface is covered, the particles, having no hold on the water but attracting each other, coalesce and precipitate. The addition of more dye forms a second monolayer but with the *ionizable* aspect of the dye molecules exposed to the water; and, since they now have a strong affinity for water, the particles disperse. Gelatin behaves in a similar manner; if a silver bromide sol is titrated with very dilute gelatin at 40° C., when the gelatin is molecularly dispersed, a precipitation point for both silver halide and gelatin will be reached. If the titration is continued with excess dilute gelatin solution, the precipitate is redispersed. The precipitation point is, however, much less easy to reproduce than with dye, very possibly owing to the longer time required by the large molecules of gelatin to arrange themselves on the silver halide particles.

This precipitating effect of a protective emulsion colloid in very small amounts on a suspension colloid has been observed in many cases [26] in a rather qualitative way and associated with a vague idea of sensitization. It was observed by Amelina, who measured the effect of gelatin on the electrokinetic potential; [27] but it is not simply a matter of the electric charge but, as in the case of the dye, of the interaction of water-resistant groups. These groups are responsible for the precipitation of gelatin from very dilute aqueous solutions at the interface with benzene.[28] This orienting factor has been indicated repeatedly by Sheppard [29] but is seldom considered in the literature of colloids.

It is generally agreed [30] that the protective substance must be strongly adsorbed to the surface of the particles protected, and it may be assumed that certain active groups are those through which attachment to the surface atoms of the silver halide is effected. While, conventionally, these groups may be assumed to form only a monomolecular layer, their effect may extend to a layer several molecules deep; in the case of gelatin, the molecular depth is probably not the length of the molecule itself but the thickness of a chain or net. Every particle of silver halide may be conceived as surrounded by a gelatin layer attached to the grain at various points by the active groups of the gelatin, which produce an inactivation of the surface of the silver halide particles, depending upon the pH and pAg values. While this protective action of the gelatin restrains flocculation, it does not prevent the growth of the silver halide grains provided that there is present a solvent for the silver halide, such as ammonia or excess of soluble halide. In this process of grain growth, the active groups of the gelatin attached to a particle are displaced by the more active solvent molecules which dissolve the silver halide in the form of a complex, and thus the particle can grow in spite of the presence of the gelatin.

It appears that a protective colloid is not essential to dispersion. Stable sols of silver halide can be prepared containing either excess positive (Ag^+) or excess negative (Br^-) ions. The charge here is regarded as assuring dispersion by the electrostatic repulsion of the charged particles. This, however, is secondary. The essential factor is the water atmosphere polarized about the ionic surface and, thus, the "homologizing" of the surface to the solvent medium.* (This aspect is brought out in a study of the reverse process of coalescence.[31]) More complete consideration of the charge of a silver halide shows that its importance is generally overemphasized. A great many statements in the literature concerning protective colloid action relative to silver halides and, particularly, gelatin are worthless because of lack of control of pAg and pH. This is particularly so as regards the protection of unexposed silver bromide from reduction by a developer.

---

* Expression of J. W. McBain.

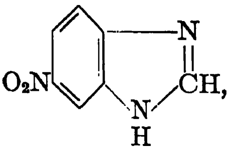
It is often stated that silver bromide precipitated from solution in the absence of gelatin and treated with a photographic developer without exposure to light is immediately reduced. In fact, by very careful sedimentation, layers of silver bromide free from gelatin may be obtained, on which developable latent images can be produced by light, although it is necessary to use very dilute and highly restrained developers. Plates coated with these sedimented layers prepared from silver halide sols were used by Schumann for the photography of the extreme ultraviolet, which is absorbed by gelatin. Lüppo-Cramer[32] pointed out that layers of this type are produced by the sedimentation from the sol condition of particles protected by external bromide ions, and that very little coagulation intervenes. Dilute stable *sols* of silver bromide prepared by maintaining an excess of bromide behave in the same way as *layers* sedimented from the sols, since latent images can be developed in them; that is, the sols show a retardation of reduction relative to that of the coagulated form of the silver bromide free from bromide ions, which is reduced immediately. Again, in this connection, the importance of the pH and pAg values must be emphasized; a gelatin emulsion at pH 4 and pAg < 5.0 is spontaneously reducible by alkaline developers; a silver bromide sol at pAg 7 $\sim$ 8 and pH $\sim$ 7, *free from gelatin*, develops a latent image free from fog.

Reinders and van Nieuwenburg[33] experimented on the effect of gelatin on the reduction of finely divided crystalline silver chloride, which they prepared by blowing air through an ammoniacal solution to remove the ammonia. They found that a concentration of gelatin as low as one part in one hundred thousand produced a notable restraint on the rate of reduction, the effect increasing with the concentration of gelatin up to

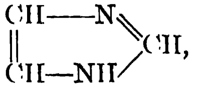
½ per cent. However, these experiments were carried out without control of pH and pAg. In their discussion, the authors assumed the reduction of silver ions in solution, whereas the reaction probably takes place in an adsorption layer on the solid phase. In this connection, reference should be made to the suggestion of Schwarz and Urbach[34] that developability results (with reducing anions) from the removal of negative charges (Br ions) from the surface of silver halide, permitting negatively charged (anionic) reducers to approach the surface (Chapter VIII, p. 319). In agreement with this may be cited the work of Lottermoser[35] on the effects of high molecular positive ions on the reducibility of silver halide sols.

The protective action of gelatin can thus be explained in terms of the definite chemical behavior of ions and molecular groupings. The true colloid functions of gelatin in photography lie in its physical properties: its mechanical support as a viscous medium in solution, in the formation of jelly which supports the grains of silver bromide but allows reagents to have access to them.

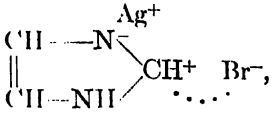
In addition to this, it has been suggested that a combination between the gelatin and silver halide takes place. All evidence in support of this is indirect, but, in view of the chemical structure of gelatin and the known relation between some of the groups contained in the amino acids and silver bromide, there may be direct chemical adsorption of gelatin to the silver halide. Sheppard[36] found that thioanilides, such as thioacetoanilide, form notably stable compounds with the silver halides, and these are not readily decomposed to silver sulfide or reduced to metallic silver. This he associates with the capacity of thioanilides to reduce fog and cut down sensitivity when added to an emulsion prior to exposure and to interfere with development if the emulsion is treated with them after exposure. He suggests that a similar action is operative in the case of the imidazole compounds, which are well known to reduce fog either if added to an emulsion or if present in the developer. Thus, nitrobenzimidazole,



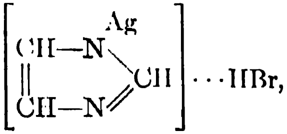
is an active antifoggant. The imidazole nucleus,



can be regarded also as attaching to silver bromide by the electrovalency of the doubly bonded nitrogen,

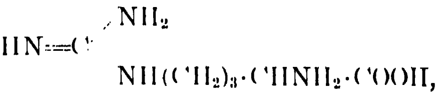


and, again, by rearranging and splitting off HBr,



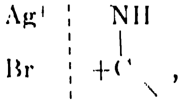
as in the case of thioanilides. The double bonds still remaining would supply a further force of residual attraction.

The amount of an actual imidazole nucleus-containing body, *viz.*, histidine, in the hydrolysis products of gelatin is quite small, not more than one per cent. The amount of arginine,



$$HN{=}C\begin{matrix}\nearrow NH_2 \\ \searrow NH(CH_2)_3\cdot CHNH_2\cdot COOH\end{matrix},$$

is, however, fairly large, 8 to 9 per cent; and since this contains the group $>C{=}NH$, it may be considered to act in the same way, that is, to be attached to silver bromide by the polarity of the double bond,



forming an oriented adsorption layer interfering with flocculation and recrystallization as well as with reduction to silver. This latter possibility becomes more reasonable if the *adsorption theory* of development is considered. In this, it is supposed that the reducing ions are *first* adsorbed, by electro- or contact-

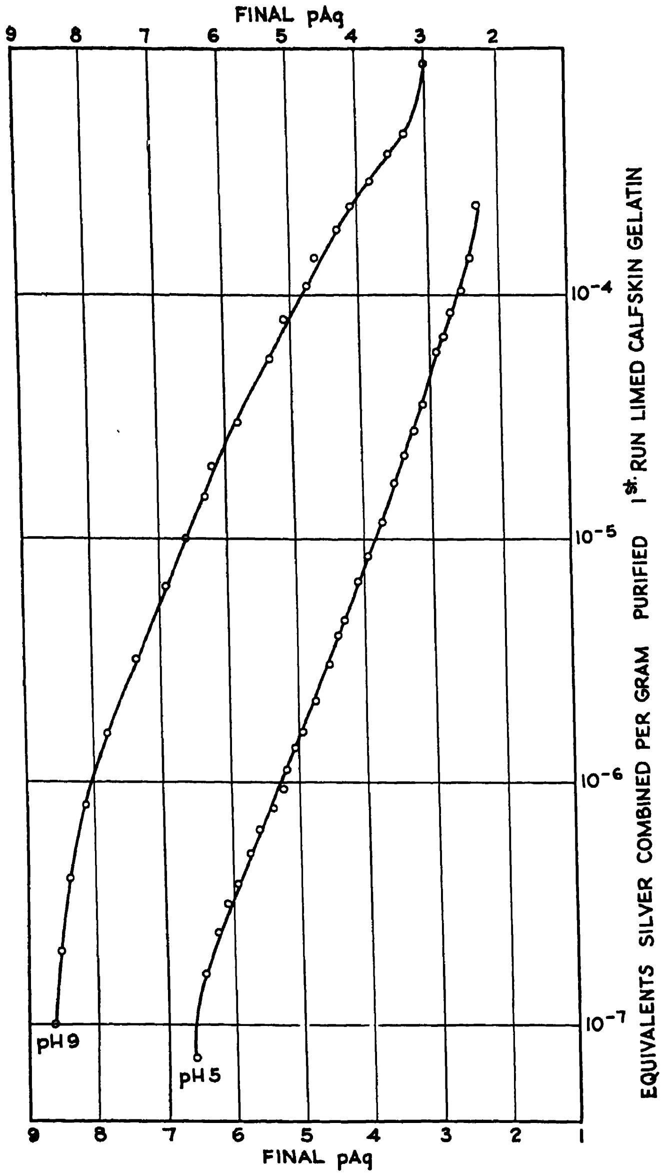


FIG. 35. Typical curves for the direct titration of purified gelatin with silver nitrate.

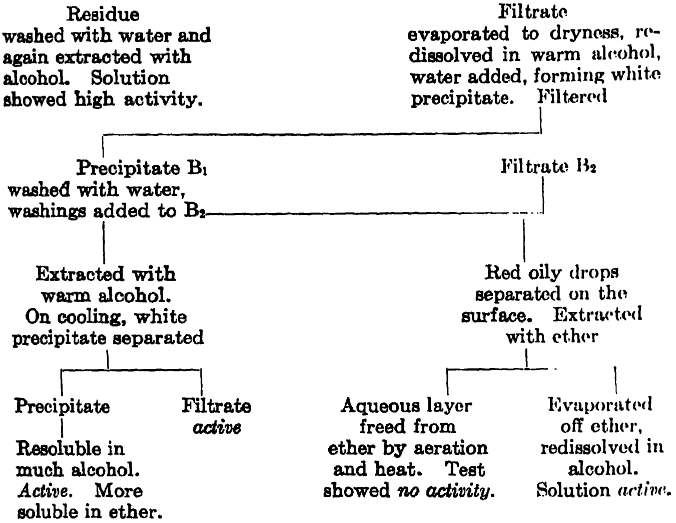
adsorption, as

$$\begin{array}{c} Ag^{+}\text{- -}\,\vdots\,\text{- -}R^{-} \\ Br^{-}\text{- -}\,\vdots\,\text{- -}Na^{+}, \end{array}$$

and that the $Ag^{+}R^{-}$ complex undergoes rearrangement *in situ*, producing metallic silver and oxidized reducer (Chapter VIII, p. 316). The structure of the silver compound with histidine is still uncertain; it may be a co-ordination compound rather than a replacement of imino-hydrogen. The mode of combination of arginine in the gelatin molecule is also uncertain; it does not begin to function basically until very high pH values and the silver-ion titration curves of *purified* gelatin (with the silver electrode) do not reveal any discontinuities or changes of slope in the pH–pAg range which is important in photography[37] (Figure 35).

Thus, apart from *specific impurities*, the silver-ion combining power of gelatin—its reduction of silver-ion activity—appears to be controlled mainly by co-ordination of silver ion and amino (and perhaps imino) groups. But, while the primary function of gelatin is to increase dispersion and produce a restraint on development, different gelatins having similar colloidal properties may have very different effects upon the sensitivity of emulsions made with them. Thus, emulsion makers select gelatins to produce the effects which they require and classify gelatins as "active" or "good," on the one hand, and "inactive" or "slow," on the other.

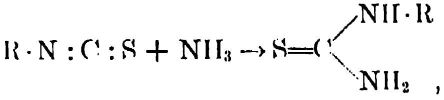
During the period 1920–1925, photographic chemists became convinced that there must be present in "good" gelatin a sensitizing substance or substances which profoundly modified the sensitivity of the silver halide grains. In 1925, Sheppard[38] published a paper in which he described the isolation of sulfur-bearing sensitizers which occur naturally in some gelatins. By selecting the gelatin samples, Sheppard was able to prepare emulsions which resembled one another in jelly strength, grain-size distribution, and general chemical composition of the silver halide grains, yet varied widely in speed, contrast, and freedom from development fog. With R. F. Punnett, he showed that an extract could be prepared from a gelatin which would produce fast emulsions which, when added to an emulsion made with a "slow" gelatin, conferred higher speed, so that the extract contained a sensitizer. Assisted by J. H. Hudson, Sheppard made a search for the sensitizing material, starting with the various stages in the process of gelatin manufacture from rawhide. During the search, it was found that the acid liquors used to *delime* the swollen hide show appreciable sensitizing power. By evaporation or by precipitation of aluminum hydroxide in the liquor, a sludge was secured which held the sensitizer. The sludge, treated with alcohol and filtered, yielded a solution and a residue, which were examined according to the diagram below:


Residue washed with water and again extracted with alcohol. Solution showed high activity.
Filtrate evaporated to dryness, redissolved in warm alcohol, water added, forming white precipitate. Filtered
Precipitate B_1 washed with water, washings added to B_2
Filtrate B_2
Extracted with warm alcohol. On cooling, white precipitate separated
Red oily drops separated on the surface. Extracted with ether
Precipitate
Resoluble in much alcohol. *Active.* More soluble in ether.
Filtrate *active*
Aqueous layer freed from ether by aeration and heat. Test showed *no activity.*
Evaporated off ether, redissolved in alcohol. Solution *active.*

The active material in the sludge from the deliming liquor was named, provisionally, *Gelatin X.* It proved to be soluble in ligroin, so that a ligroin extract could be used for further investigation. This extract dried down to a reddish wax consisting chiefly of cholesterol, which was at first thought to be the sensitizer. However, pure cholesterol from other sources proved photographically inactive. The search was continued for an impurity in the cholesterol. The substance might be an associated sterol, or it might be some quite unrelated body. As sources of sterols, vegetable seeds appeared more convenient than glue liquors, and here the harvest was plentiful. Beans, peas, cereals, and even alfalfa yielded potent extracts. The sensitizer appeared to be associated with phytosterol but was not itself a sterol because it was found to be shared in varying degrees between the sterol and certain solvents. Eventually, a concentrate was obtained from black mustard seed which was so much more effective than the other extracts that "Gelatin X" became reasonably identified as allyl mustard oil or some compound closely related to it.

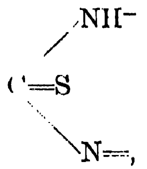
Following this broad clue, the combinations of the allyl radical with radicals containing sulfur and other likely elements were examined to locate the source of the activity. It became apparent that only the isothiocyanate group has sensitizing power and that the mere presence of sulfur, *per se*, was not sufficient. The sensitizers were intensely active, quantities varying from one to three parts in a million exerting a measurable effect on emulsion speeds. It is little wonder that such minute traces had long escaped detection in photographic gelatin. Following the discovery of plant seeds as an independent source, the sensitizer was again isolated from deliming liquors and shown to be similar to allyl isothiocyanate or allyl thiocarbimide.

The mode of interaction with silver salts was then investigated.* The sensitizer is effective only in the presence of alkali sufficient to produce ammonia or free amino groups with which it reacts to form thiocarbamide:



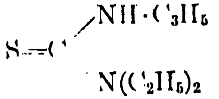
$$R\cdot N:C:S + NH_3 \rightarrow S{=}C\begin{array}{l}\diagup NH\cdot R\\ \diagdown NH_2\end{array},$$

and it was found that any organic substance containing the grouping



$$C{=}S\begin{array}{l}\diagup NH-\\ \diagdown N{=},\end{array}$$

such, for instance, as allyl diethyl thiourea



$$S{=}C\begin{array}{l}\diagup NH\cdot C_3H_5\\ \diagdown N(C_2H_5)_2\end{array}$$

can act as a sensitizer.

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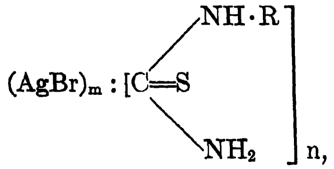
* The action of the sensitizer with the silver bromide and its effect upon the sensitivity of the emulsion are discussed more fully in Chapter IV, p. 153.

The first stage in sensitizing, therefore, is the conversion by ammonia or an amino body to amide of any sulfur-bearing material available in imide form. The small amount of thiocarbamide in the emulsion then attacks the grains and forms small areas of an addition compound:



$$(\mathrm{AgBr})_m : \left[\mathrm{C}\begin{matrix}/\mathrm{NH\cdot R}\\ =\mathrm{S}\\ \backslash\mathrm{NH_2}\end{matrix}\right]_n,$$

where m and n are simple integers; in the most important case, $m = n = 1$. When this compound reacts with alkali, it is converted into silver sulfide.

Sheppard's work established definitely the importance of alien sulfur compounds in gelatin, which produce silver sulfide on the silver halide grains during the making of the emulsion. The effect of this silver sulfide in producing an increase of sensitivity on the grain is discussed later (Chapter IV).

Following Sheppard's discovery, it became evident that the amount of labile sulfur in gelatin is of the utmost importance in relation to its photographic properties. Evidently, much depends upon the criterion of lability and, in turn, upon the analytical method. The criterion here is the formation of silver sulfide under specific conditions. Sheppard and Hudson[39] worked out a method for the determination of the total sulfur in proteins and for the determination of the labile sulfur, that is, the sulfur which forms silver sulfide under certain definite conditions, involving the microchemical determination of the sulfide ion. The principle of the method is the decomposition of the sulfur-containing body with an ammoniacal solution of silver chloride to form silver sulfide. The silver sulfide is quantitatively decomposed with concentrated hydrochloric acid to form hydrogen sulfide, which is driven off by a current of nitrogen and absorbed by p-aminodimethylaniline solution to form methylene blue, this being estimated colorimetrically.

This method can be considered only as an over-all or breakdown method. The high temperature and high alkalinity make sulfur reactive to silver which would not react under the milder conditions prevailing in emulsion preparation. The method, however, has been modified by Sheppard and Ballard to determine the silver sulfide (and silver) formed on grains in normal emulsion-making procedures.[10] It may be noted that cystine-bound sulfur must be reduced by such powerful agents as sodium stannite before it will react completely with silver ion to form silver sulfide. It is improbable that either cystine or cysteine sulfur in gelatin reacts in emulsion-making to form silver sulfide, but some of it appears to react under the conditions of the original Sheppard and Hudson procedure. Again, it is desirable to make a determination of sulfide-ion sulfur on a separate sample by aeration of the acidified solution of gelatin and absorption of any hydrogen sulfide. This sulfide sulfur appears to be associated with the formation of colored fogs. Excess of labile sulfur of the silver complex forming type tends to produce black or normal chemical fog.[11] Colored fogs are due to nuclei of silver sulfide separated from the grains, which act as centers of physical development. The over-all analytical method was studied by Bekunoff,[12] who adopted it with slight modifications. Bekunoff and Chibisoff [13] found a relation between the total labile sulfur in a gelatin and its tendency to produce colored fog if the emulsion is developed without bromide.

The discovery of the presence of alien sulfur compounds in gelatin and of the importance of the labile sulfur content did not, however, clear up entirely the riddle of the behavior of different types of gelatin used for making emulsions. The labile sulfur in gelatin exists in various forms, some of which aid in the production of sensitivity, while others tend to produce dichroic or general fog. In addition to this, gelatin undoubtedly contains antifogging and desensitizing components. These may be of the nature of imidazoles or azines, in accordance with the discussion by Sheppard mentioned above. At the present time, so many compounds are known to have antifogging, stabilizing, or desensitizing effects that it is probably impossible to limit to these two classes of compounds the traces of foreign substances which may occur in so complex a material as gelatin.

Within the last few years, a great number of substances have been discovered to be effective in controlling fog and stabilizing the grain sensitivity of emulsions, and some of these may be present in gelatin. A paper by Makaroff, Pobedinsky, and Pulina [44] summarizes the matter fairly well. They divided gelatins into classes according to their content of foreign substances and attempted to define these classes by the changes which occur in the properties of the emulsion during its preparation. The authors claim that the quality of a gelatin can be evaluated by the γ * at the end of the first ripening, by the increase in the light-sensitivity in the second ripening, and by the increase in γ during the second ripening, the second ripening taking place after washing and, therefore, in the presence of very small amounts of free bromide. Using these criteria, the authors classify gelatins as follows: (it must be remembered that the emulsion-making method used is that involving the use of free ammonia):

Class I. The gelatin contains a small amount of sensitizing material and no desensitizing material. The emulsion has a low γ value after the first ripening. During the second ripening, a considerable increase of light sensitivity and γ occurs. Such gelatins produce emulsions of high light-sensitivity.

Class II. The gelatin contains a small amount of desensitizing substance and possibly slightly more sensitizing material than gelatins of the first class. The emulsions have a slightly higher γ value after the first ripening. Sensitivity increases very little during the second ripening. Such gelatins produce emulsions of moderate sensitivity.

Class III. The gelatin contains a small amount of sensitizing material and a large amount of desensitizing material. The emulsions have a high γ value after the first ripening. The sensitivity decreases somewhat during the second ripening. Such gelatins produce emulsions of low sensitivity.

Class IV. The gelatin contains a large amount of both sensitizing and desensitizing materials. The emulsions have a high γ value and show considerable fog after the first ripening. The light-sensitivity is appreciably lowered during the second ripening. Such gelatins produce emulsions of low sensitivity and high fog.

According to the Russian workers, therefore, photographic gelatins can be classified not only by analysis for labile sulfur and cystine, as well as for free sulfhydryl compounds, but by the change of sensitometric values which occurs during emulsion-making.

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* γ is the slope of the straight line portion of the "characteristic curve" (Chapter V).

The physical aspects of the matter are discussed by Chibisoff.[45] He considers that the most characteristic feature of the first ripening is the increase in size and decrease in the number of grains, which causes a drop in the γ value during ripening. Thus, with any gelatin, the sensitivity of the emulsion increases during the first ripening, while γ drops. The characteristic of the finishing, or second, ripening is the changed condition of the surface of the grains, which involves a complex change in sensitivity; but, since any change in the surface is identical in grains of different sizes, a simultaneous change of the γ value is noted. Thus, an empirical rule can be formulated from the increase in sensitivity and the change in γ by which the properties of the gelatin can be stated.

The conclusions of Chibisoff have been criticized by Trivelli and Smith,[46] who prepared emulsions with a standard gelatin and then used various gelatins for setting and ripening after washing. They applied the Bravais-Pearson correlation coefficient to the relations between the value of γ before washing and the rise of γ in digestion, and those between the value of γ and the rise of sensitivity. They found that the first relation showed strong correlation but that the increase of sensitivity during after-ripening is not related to the value of γ obtained in the unwashed emulsion.

In an answer to this criticism, Chibisoff[47] considers that Trivelli and Smith should have used the gelatin under test throughout the emulsion-making process instead of using a standard gelatin for precipitation.

The classification of gelatins given above is necessarily speculative because it is not possible to give independent values for the sensitizer inhibitor ratios and absolute values. In fact, it is possible to:

(1) increase the sensitizer content while keeping the antisensitizer constant although unknown in amount. Sheppard[41] found that this produces an initial increase in both speed and γ, followed by a period of constant γ and increasing speed, and a subsequent period of decreasing speed and γ (with rapid increase of fog);

(2) remove simultaneously most of the adsorbable sensitizers and foreign inhibitors (non-gelatin). This is effected by pretreatment of the gelatin with silver halide. Sheppard[40] found that this produces a continued increase in speed without appreciable change in γ, which remains very low. The time of development is prolonged, however, beyond practical limits;

(3) remove the inhibitor, with an independent adjustment of the sensitizer. The immediate effect of this for comparable digestion times and temperatures is to increase both speed and γ.

The modification of gelatin by treatment with silver bromide, silver sulfide, and silver is discussed by Chibisoff and Mikhailova.[48] They conclude that gelatin contains substances one group of which have an influence upon the dispersion of the silver halide precipitate, while other materials act as sensitizers during the digestion of the emulsion.

Silver bromide and silver sulfide adsorb substances from the gelatin selectively and thus affect the properties of emulsions made with it. Metallic silver also changes the properties of the gelatin, inhibiting the Ostwald growth of the halide grains during the ripening of ammonia emulsions. The gelatin is so affected that it becomes soluble in alcohol.

THE HARDENING OF GELATINS AND EMULSIONS

By the *hardening* of gelatin is meant a process similar to the tanning of rawhide (formation of leather), which produces (1) a reduction of swelling in water and aqueous solutions and (2) an increase in the temperature required for solution in water —the so-called *melting point* (M.P.). The hardening also produces an increase of the apparent viscosity of gelatin solutions and a rise in the temperature at which jelly forms—the *setting point.* The methods of measuring melting point are necessarily arbitrary, involving a definite rate of heating and definite agitation. Swelling may be measured by the change of either weight or volume as, for instance, by the water absorbed, calculated as a percentage of the gelatin present. Certain other practical criteria of photographic hardening are mentioned later.

As an indication of "hardness," Berczely[49] and Elöd[50] used a wash-off period, the time required to wash the gelatin from an adherent substrate with a regulated spray of water of constant temperature. This method does not seem to have much advantage. Apart from the uncertainty of an end-point, the temperature of the wash water must be adjusted to different values corresponding to M.P., for various degrees of hardening.

Gelatin is derived from the collagen of hide by processes which do not involve any very considerable chemical change, and the fundamental chemical reactions between tanning agents and collagen are much the same as between these tanning agents and gelatin. There are, however, certain important differences. These arise both from the actual physico-chemical differences between hide and gelatin and from the difference in the use of the product. Hide contains, besides collagen, proteins hydrolyzable with more difficulty, such as elastin and reticulin; and it has a microscopic fibrous and porous structure which is absent in gelatin. In tanning, while there is an intimate reaction of tanning reagents with the interior of the fibers, perhaps the more important phase is the external protection of the fibers against hydrolysis and the deposition of water-proofing colloidal material in the interstices between the fibers and fibrils. In the hardening of photographic gelatin, such a deposition is permissible to only a slight degree, since it would lead to turbidity and loss of transparency. While some hardening reactions, therefore, are the same in principle as tanning reactions, limited in degree and range, other reactions of tanning agents cannot be used in gelatin hardening. Furthermore, the collagen is usually comparable with lime-processed gelatin, while gelatin may also be obtained by purely acid processing (p. 61).

Photographic materials are hardened at two points for different purposes:

1. They are hardened during manufacture to give protection against softening and sticking at high temperatures and humidities. This requires hardening of the gelatin emulsion prior to coating. The hardening agents and products must not affect the sensitivity and other photographic qualities. Also, the hardening should not increase greatly with the keeping of the material and must not affect the speed of development or the life of the latent image.

2. The material is often hardened during processing to keep the wet gelatin firm and undisturbed throughout the processing

operations. This is especially necessary if the processing is carried out at temperatures higher than normal. Elevated temperatures tend to produce softening, solution, and hydrolysis of the gelatin; hardening is not a complete protection, because a combination of hardening and softening actions leads to reticulation (see p. 85). Since most hardening reactions have a high temperature coefficient (*v. inf.*), reticulation occurs in hardened gelatin treated with solutions or water (particularly at pH and

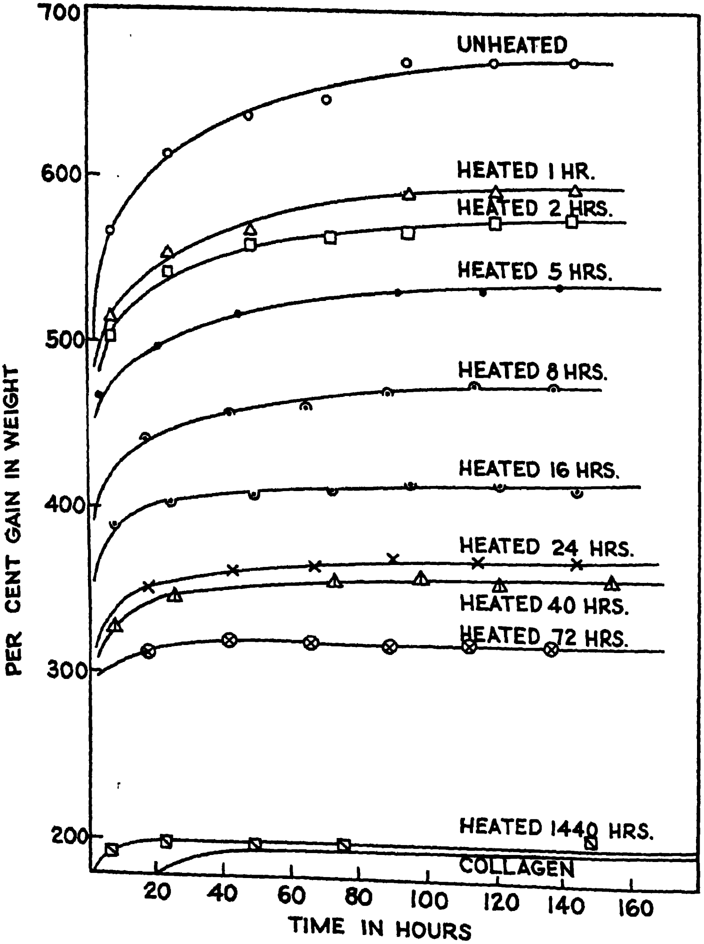


FIG. 36. Curves showing the effect on water absorption of heating gelatin at 105–110° C.

other conditions favoring swelling) at higher temperatures. In general, hardening agents may be introduced into the emulsion prior to coating, before development or during development, between development and fixation (in stop baths), in the fixing bath, and after fixation.[51]

Gelatin may be hardened by simply heating it in the dry state. Hofmeister [7] found that gelatin heated for several hours at 130° C. could be dissolved only by boiling for hours. Bogue [52] made a similar observation on glue. A study of the effect was made by Sheppard and Houck,[53] who measured the hardening by determining the water absorption at 15° C. from a buffer solution (0.001 N acetic acid—sodium acetate) at pH 4.95, this being the isoelectric point of the gelatin. The results of heating at 105°–110° C. are shown in Figure 36. It is seen that the water-absorption values (at swelling limit) decreased steadily with time of heating and approached a limiting value, after heating for two months, of 200 per cent. The value for lime-processed collagen also is about 200 per cent at 15° C. Gelatin brought to this state is insoluble in water at 70° C. for ordinary periods of time. After even five hours' heating at 110° C., it is incompletely dissolved by hot water.

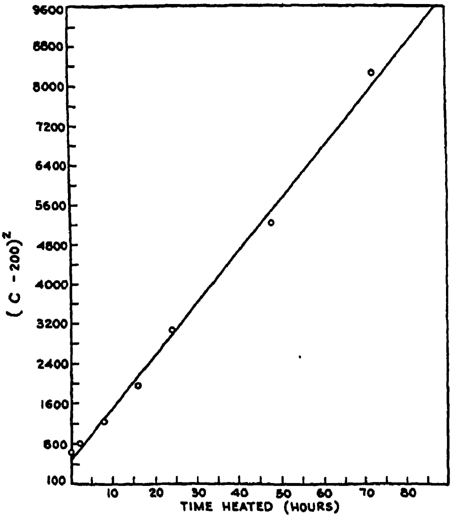


Fig. 37. Relation between $(C - 200)^2$ and the time of heating.

As the reaction variable, proportional to the concentration of original gelatin, Sheppard and Houck used the equilibrium percentage regain in weight by the absorption of water for a sample of gelatin heated for time t minus the equilibrium percentage regain after heating for infinite time, $C - C_\infty$; for C_∞, the value was 200, as stated. A graphic analysis of the reaction curves showed that plots of $(C - 200)^2$ against t give straight lines

(Figure 37). This corresponds to

$$\frac{1}{x^2} = kt;$$

hence,

$$\frac{dx}{dt} = k(a - x)^3,$$

as for a termolecular reaction. This expression is valid for temperatures from 90° C. to 116° C. It is believed to be valid below 90° C., but the rates of reaction are too low to make measurements possible. At higher temperatures than 116° C., the gelatin became yellow and showed signs of decomposition and charring.* The values of the velocity constants at different temperatures are as follows:

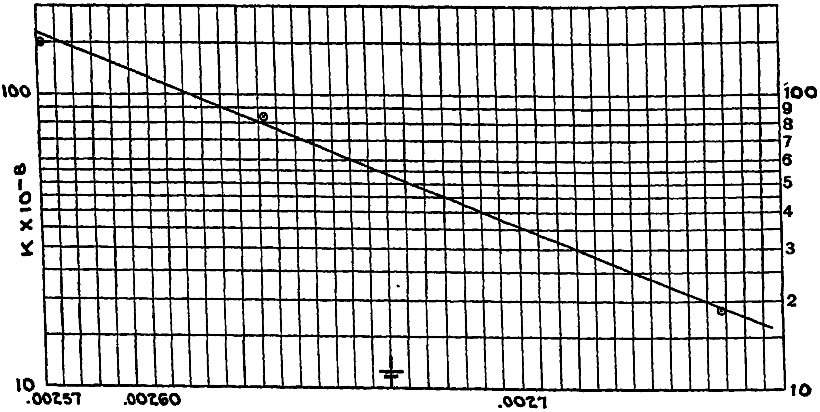


FIG. 38. Rate of change of the velocity constant of insolubilization of gelatin with temperature.

Temperature	k
90° C.	18.6
107°	84.4
116°	150.0

Applying the Arrhenius expression for the effect of temperature on the rate of reaction,

$$\frac{d \log k}{dt} = \frac{A}{RT^2},$$

---

* Probably the measurements should be repeated in the absence of air.

in the integrated form,

$$\log \frac{k_1}{k_2} = \frac{A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

the constant A equals the slope of the graph of $\log k$ vs. $1/T$ multiplied by 2.303×1.98 (Figure 38). This gives $A = 23{,}160$ calories as the heat of activation of the gelatin.

PHOTOCHEMICAL HARDENING

A further justification for the end value of 200 is obtained from data on the insolubilization of gelatin by ultraviolet light, which was followed by Brintzinger and Maurer,[54] who measured the reduction of swelling. Using the limit value of 200, a fair approximation to the termolecular expression was obtained (Figure 39). The equivalent temperature, corresponding to the high velocity indicated, is much higher than that to which gelatin can be heated (in the presence of air) without decomposition. But many photochemical reactions correspond to thermal reactions at unrealizable temperatures, because with heat many side reactions are stimulated, which the selective absorption of light does not produce. The hardening of gelatin by light of wave

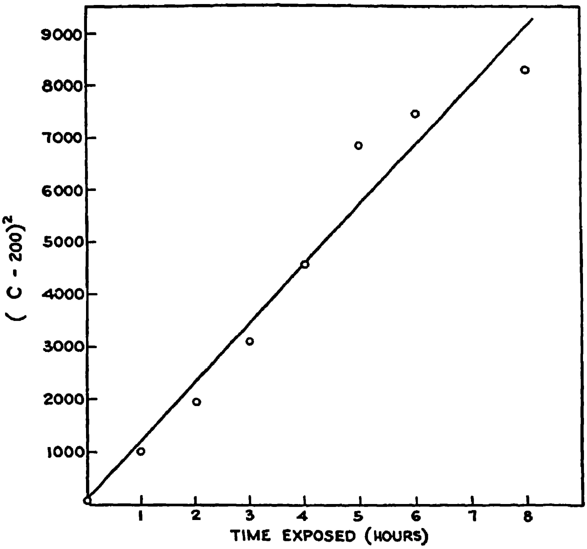


FIG. 39. Insolubilization of gelatin by ultraviolet light.

lengths shorter than 300 mμ is of considerable importance, as indicating which molecular groups in gelatin are concerned with insolubilization.

The self-hardening of gelatin may have a definite connection with that produced by light as well as by inorganic and organic reagents. An interesting observation of this is reported by Galinsky.[55] She states that exposure to light of a gelatin solution containing dichromate, followed by precipitation with acetone, gave an insoluble ash-free gelatin, *i.e.*, containing no chromium. This gelatin was chemically indistinguishable from the original soluble gelatin. The bichromate appears to have acted as an optical sensitizer for a reaction which otherwise requires ultraviolet light.

The hardening of gelatin (and fish glue) containing dichromate by exposure to light absorbed by the dichromate is the basis of important photocopying and photomechanical processes and has been the subject of considerable investigation. The experiment just referred to suggests that an optically sensitized process (similar to that produced directly by ultraviolet light) may be playing a part. It has also been suggested that oxygen, split off from the chromic acid by the light and accepted by gelatin, might be the effective agent according to a reaction of the type

$$\mathrm{CrO_3} + h\nu \rightarrow \mathrm{CrO_2} + \mathrm{O}$$
$$\text{Gelatin} + \mathrm{O} \rightarrow \text{Insoluble gelatin.}$$

A more general opinion, however, is that the insolubilization is produced by a reduced chromium compound, corresponding to $\mathrm{Cr^{III}}$, *e.g.*, $\mathrm{Cr_2O_3}$, and, therefore, is the same in principle as the chrome hardening noted later, This view was supported by A. and L. Lumière [56] after its proposal by Eder.[57] In terms of the chromic acid, the photochemical reaction can be represented by

$$\mathrm{H_2Cr_2O_7} \rightarrow \mathrm{Cr_2O_3} + \mathrm{H_2O} + 3\,\mathrm{O}.$$

It should be remembered that chromate and dichromate ions are in an equilibrium depending upon pH according to:

$$2\,\mathrm{CrO_4^{=}} \underset{\mathrm{OH^-}}{\overset{\mathrm{H^+}}{\rightleftharpoons}} \mathrm{Cr_2O_7^{=}}.$$

The evidence of Lumière, Lumière, and Seyewetz for Cr_2O_3 being the actual hardening agent was based chiefly on analyses of hardened gelatin withstanding boiling water. Eder had suggested that an intermediate oxide, corresponding to chromous chromate, might be formed by the combination of Cr_2O_3 with excess CrO_3, giving $Cr_3O_6 = (CrO_2)_3$, but analytical evidence for this is slight and inconclusive. An expansion of the chromium oxide, Cr_2O_3, conception along colloid chemical lines was made by Mayer,[58] who followed the change of electrical conductance with exposure. The bichromate is used at such an acidity that the over-all change may be represented as

$$2\,H^+ + Cr_2O_7^{--} \rightarrow Cr_2O_3 + H_2O + 3\,O.$$

There is, therefore, a large reduction of the number of hydrogen ions; and the conductivity falls rapidly with exposure to light.

The hardening of gelatin by exposure to light in the presence of certain dyes was observed by Meisling.[59] The dyes used were erythrosin and auramine. Generally, the hardening was not very pronounced but sufficient to give a wash-off effect with the moist jelly at about 32°–37° C. The sensitivity was about the same as for dichromate. Meisling thought that formaldehyde is formed by the action of light on the dye, but he presented no analytical evidence of this. It is uncertain whether there is true optical sensitizing or indirect action by products of the photolysis of the dye. Little or no dark hardening was observed.

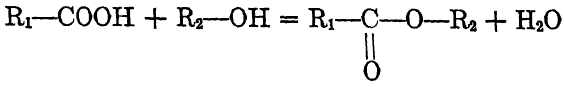
Hardening processes involving the decomposition of diazo compounds in gelatin, in which the products have a tanning action, are described.[60]

THE MECHANISM OF THERMAL AND PHOTOCHEMICAL INSOLUBILIZATION

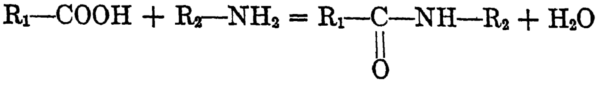
Hofmeister attributed this change to a reversal of the hydrolysis of collagen to gelatin, which he expressed by the equation

$$\underset{\text{collagen}}{C_{102}H_{149}O_{38}N_{31}} + H_2O \rightarrow C_{102}H_{151}O_{39}N_{31}.$$

Apart from the fact that the empirical formula has little justification, the measurement of 1 part of water in some 140 parts of gelatin has no significance. Actually, the insolubilization continues when no further loss of weight can be measured.[54] This does not prove that a splitting off of water molecules by condensation between OH-containing groups does not occur, because the binding or primary adsorption of water to soluble gelatin is so powerful[17] that the split-off water might be retained in such fashion. Hofmeister's conception of a reversion to collagen is not to be lightly dismissed, though not expressible in so simple a fashion as he suggested. If gelatin jelly strips containing large proportions of alcohol, glycol, or glycerol are stretched some 200 to 300 per cent and dried, the almost entirely amorphous X-ray diffraction pattern of the unstretched gelatin changes to an imperfect fiber diagram very similar to that given by collagen.[61] Such strips do not show any difference in total water absorption from unstretched gelatin. But, corresponding to the orientation of the gelatin molecules and crystallites thus induced, the swelling (absorption) in the direction of stretch is greatly reduced; that in directions perpendicular thereto, increased.[62] If, however, such superstretched strips are thermally insolubilized, the total water absorption sinks to near that of lime-processed collagen. Sheppard and Houck pointed out also that the termolecular order of the thermal hardening reaction may be significant, as it appears that for reduction of the total water absorption a reaction in three dimensions is necessary. This might be regarded as the formation of cross condensation or polymerization in three dimensions. Cross condensations of the type



$$R_1{-}COOH + R_2{-}OH = R_1{-}\underset{\underset{O}{\|}}{C}{-}O{-}R_2 + H_2O$$



$$R_1{-}COOH + R_2{-}NH_2 = R_1{-}\underset{\underset{O}{\|}}{C}{-}NH{-}R_2 + H_2O$$

have been suggested by Speakman and Hirst[63] for the action of acids on wool fibers, but the nature of the cross linkages is speculative. The conclusion appears justifiable, however, that the conversion of (lime-processed) collagen to gelatin involves something more than the disorientation of long-chain molecules assembled in crystallites (p. 62). Hydrolytic disruption of definite chemical interlinkages may occur between the long-chain macromolecules. Another alternative might be disruption of intermolecular hydrogen bridges, such as may be assumed in cellulose micelles or crystallites. But there are many reasons to believe that actual ester linkages (between —COOH and R—OH) occur in these, analogous to the cross linkages suggested in collagen and thermally hardened gelatin.

The thermal hardening of gelatin might also depend upon a heat coagulation of dispersed albumin in the gelatin.[9] The amount of albumin appears too small, however, and experiments have shown that the addition of egg albumin does not affect the process. Small amounts of formaldehyde, produced by oxidative processes on heating, may have an effect, but this requires further investigation.

INORGANIC HARDENING AGENTS

A considerable number of inorganic compounds induce permanent hardening of gelatin (and tanning of hide). The following list is not exhaustive but includes the more important substances and emphasizes the significance of polyvalency:

A		*B*
Polybasic oxides		*Polyacid oxides*
Al^{+++}	Al_2O_3	Mixed (hetero) polyacids
Cr^{+++}	Cr_2O_3	Chromates
Fe^{+++}	Fe_2O_3	Iso-compounds, such as
Th^{++++}	ThO_2	(SiO_2) Metasilicic acid
Zr^{++++}	ZrO_2	(P_2O_5) (Hexa-) metaphosphoric acid
Ti^{++++}	TiO_2	(WO_3) Metatungstic
Ce^{++++}	CeO_2	(MoO_3) Metamolybdic
UO_2^{++}	UO_3	(V_2O_5) Metavanadic

For photographic processing in hot seasons or tropical climates, "temporary hardening" is used. This consists in loading the solution, whether acid or alkaline, with a neutral salt[64] to depress the swelling and thus prevent peptization or mechanical injury. The equivalent process in tanning hide, usually carried out in acid solution, is termed *pickling*. Sodium sulfate is commonly used. The theory of the process is discussed by Procter,[65a] Procter and Wilson,[65b] and Küntzel.[66] The former authors treat it from the standpoint of the Donnan equilibrium (p. 79); Küntzel regards their treatment as inadequate since it assumes complete ionization of the protein-acid or protein-base compounds. Apart from its practical use, the procedure is of theoretical interest as regards inorganic hardening proper, from which it differs by reason of its ready and complete reversibility. A similar, reversible hardening is produced by the addition of organic solvents having no swelling or solvent action upon gelatin but being miscible with water. Examples are the lower aliphatic alcohols and water-miscible ketones.

Certain general features are common to the inorganic hardeners and are best illustrated by particular cases: Aluminum is intermediate to some extent between temporary and permanent hardening, and its chemical behavior is simpler than that of chromium. It is used mostly in the form of potash alum, $K_2Al_2(SO_4)_4 \cdot 24H_2O$, a well-crystallizing double salt of constant composition and not so rapidly affected by hydrolysis as the single salts. It is widely used in acid fixing and hardening baths, the chemistry of which was investigated by Sheppard, Elliott, and Sweet,[64a] from whose paper certain results are abstracted:

The melting point of a lime-processed gelatin was measured as a function of pH for alum hardening baths of varying concentration, and the results are shown in Figure 40. In the absence of alum, the maximum M.P., 34° C., was at the isoelectric point of the gelatin, pH 4.8. The M.P. increased with the concentration of alum, the maximum being at about pH 3.8–4.0. It might be thought that the effect is due partly to the amphoteric character of gelatin and partly to a change in the alum solution with increasing pH. The evidence is that the latter is predominant. In hardening by bathing, the actual hardening agent must penetrate the jelly. Upon the addition of alum to gelatin solutions adjusted to varying pH values, the results shown in Figure 41 are obtained. It is seen that the pH of maximum hardening had a value of 6.

In explanation of this progression, it is recalled that the amphoteric gelatin with increasing pH becomes increasingly anionic, or negatively charged. Chemically, the free —COOH groups of the end and side chains are increasingly ionized, and one may suppose that an increased degree of combination between positively charged aluminum and carboxyl ions is taking place. But, with increasing pH, the Al^{+++} ions become insoluble hydrous alumina, $Al_2O_3 \cdot x(H_2O)$.[67] The first-formed particles remain colloidal; Britton * observed actual opalescence at pH values as low as 4.2 on titrating aluminum salts with NaOH and $Ca(OH)_2$, but not below pH 4.7 with $Ba(OH)_2$; but, at pH 6.5, complete precipitation (coagulation) occurred at 1.88 to 1.92 equivalents. It is seen that the coagulation point occurs somewhat earlier than the equivalence point (3 equivalents).

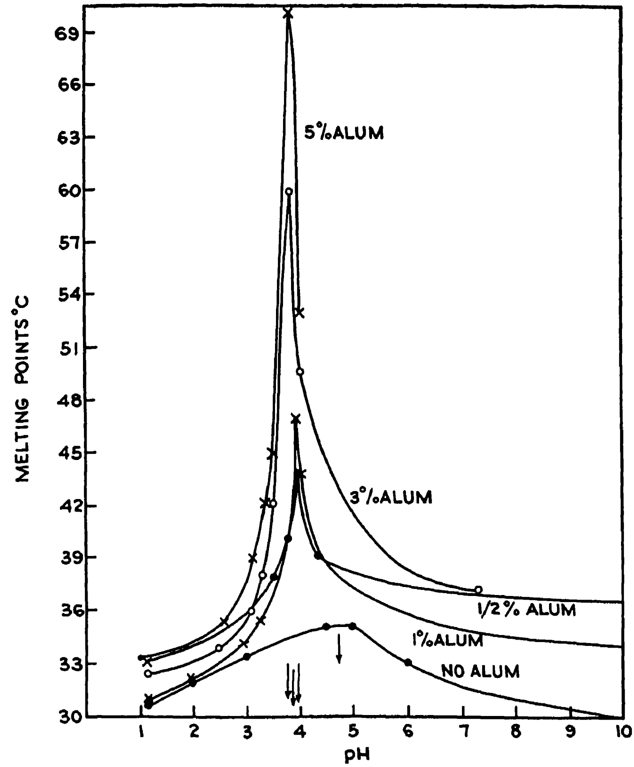


FIG. 40. Melting points of gelatin hardened with alum in relation to the pH value.

Sheppard, Elliott, and Sweet explained the hardening maxima in the gel state at pH ~ 4.0 and in the sol state at pH 6.0 as follows: In hardening by an outside bath (gel state), colloid particles of hydrous alumina are formed at pH = 4.0; the aluminum ions are retained by adsorption and prevented from diffusing into the gel. On the other hand, if the aluminum salt

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* For about 0.35 equivalents of Al for sodium hydroxide and calcium hydroxide, but 1.92 equivalents for barium hydroxide.

is mixed with the gelatin sol and the pH adjusted, hardening does not occur until near the point of actual coagulation of alumina, which is about pH 6.5. Above this, the alumina tends to be negatively charged and is unable to react with the negatively charged gelatin. It is probable that the principal reaction is between aluminum ions, Al^{+++}, free or adsorbed to hydrous alumina, and $—COO^-$ groups of the gelatin, with the formation of cross linkages between chain molecules.

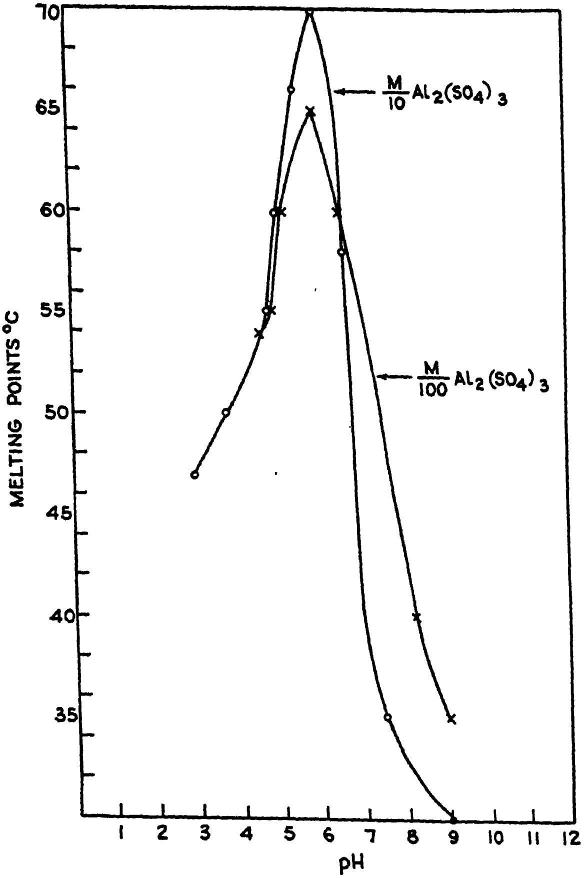

FIG. 41. Relation between the melting points and pH of gelatin solutions containing alum.

The addition of polycarboxylic ions, such as citric acid, or of hydroxycarboxylic acids, such as lactic acid, inhibits hardening by binding the aluminum ions in complexes.[64a] Pauli[68] suggested that the sols of hydrous alumina involve the formation of basic or oxy-acid salts, *e.g.*, $[m\,\mathrm{Al(OH)_3}.n\,\mathrm{AlOCl.AlO}]^+\mathrm{Cl}^-$, but there is no direct evidence for these. Thomas and Whitehead[69] supposed that "olated" and "oxolated" aluminum complexes of the Werner type (formed by interaction of the inner co-ordination spheres of aluminum ions) are formed intermediately, but X-ray study of the hydrolysis of aluminum salts[70] does not support this hypothesis. The behavior of aluminum with poly- and oxy-carboxylic acids suggests that co-ordination by chelation (giving ring formation) very possibly takes place.

The separation of hydrous oxide at a characteristic pH appears to be a general factor determining the limiting pH practicable for hardening gelatin or tanning collagen with inorganic reagents. This is illustrated by the following table:

TABLE VI

Substance	*pH of Initial Precipitation*	*pH of Maximum Hardening*	*pH of Tanning*
Al as $Al_2(SO_4)_3$	4.1 ~ 4.2	4.0 gel 6.0 sol	4-6
Cr as $Cr_2(SO_4)_3$	5.2 ~ 5.3	5.1 sol	4.5-5
Fe as $Fe(NH_4)(SO_4)_2$	2.3		(2.3-3.6)
Th as $Th(NO_3)_4$	3.5 ~ 3.6	3.4 sol	(3.5-4)
UO_2 as $UO_2(NO_3)_2$	4.2		4.1-5
Ti as $Ti(NO_3)_4$	~ 2.3		~ 2.3
Zr as $Zr(NO_3)_4$	~ 2.0	~ 1.8	

The same principle in reverse applies to the anionoid radicals or acidic oxides. *Below* a certain pH, these substances precipitate as hydrous oxides. They form negatively charged polyacid anions in the soluble state above the pH at which they coagulate. The first-formed hydrous oxide particles, however, adsorb these anions, preventing penetration into gelatin. Above the isoelectric point of lime-processed gelatin at pH 4.8, the gelatin is increasingly negatively charged also, so that combination is prevented. Hence, hardening is increased at first as the pH is diminished from, say, pH ~ 10, and reaches a maximum generally while the pH is still above the isoelectric point of gelatin.

Besides aluminum, only chromium is of great importance in photographic hardening, as in tanning. The technical importance of chrome tanning in the leather industry has resulted in an enormous literature on both the practice and theory of the process.

In chrome chemistry, *basic compounds* and *solutions* are frequently mentioned. Primarily, they are simply empirical terms for materials in which there is a stoichiometric excess of Cr_2O_3 (or Cr^{III}) above the amount which would be equivalent at normal valency. This specification in terms of composition is essential; their constitution is another matter. "Violet" and "green" salts are also discussed, and contradictory statements are made concerning their relative hardening efficiency. For example, an aqueous solution of ordinary crystallized "violet" chrome alum, $K_2Cr_2(SO_4)_4 \cdot 24H_2O$, is violet, but after boiling for two hours the solution becomes green. Hardening tests show that the violet solution produces much stronger hardening.[51b] If, however, a violet solution of chromium chloride, Cr_2Cl_6, is boiled to a green solution, it will produce equal or greater hardening than the original violet solution. Actually, the criterion is the pH of the system. The sulfate or alum upon boiling hydrolyzes, splitting off sulfuric acid, and the pH is lowered. If the pH is raised again with alkali to about 4, the green sulfate will harden as well as the violet one. Hydrochloric acid evaporates from the chloride, and the pH is not lowered so much. By the reduction of dichromate with sulfur dioxide, a green "basic" chrome alum may be obtained, which, per equivalent of chromium, has greater hardening power than the normal violet alum. This "basic" hardener lacks slightly less than one fourth of its formula weight of sulfuric acid, as shown by titration with alkali. While the continuous titration curve of violet alum does not show any significant change of slope until three equivalents are approached, discontinuous or stepwise titration, with tumbling for twelve hours, gives a curve with a break at a point close to one equivalent. The continuous titration of the green (boiled) solution shows this inflection at once at about the same value, while stepwise titration of the green solution shows the inflection fairly sharply at 1.0 equivalent. This agrees with the observations of Britton [71] and suggests that definite soluble basic salts of chromium are formed having the formula $CrOHX_2$, where, for example, $X = Cl$ or $\frac{1}{2}SO_4$.

The chemistry of the chrome tanning and hardening processes has been, and still is, the subject of controversy. On the one hand, there is the Werner complex co-ordination theory of the constitution of chrome salt solutions described by Gustavson [72] and Wilson.[73] This assumes that the change from "violet" to "green" and basic solutions is caused by substitutions in the inner co-ordination sphere of the Cr^{III} atom and regards tanning and hardening as continuations of the processes of penetration and addition-compound formation. On the other hand, the colloid adsorption theory, described by Britton [74] and Weiser,[75] postulates the formation of colloidal (hydrous) oxide, which with adsorbed chromium and other ions forms a typical colloidal electrolyte. This is supposed to produce the tanning of collagen and hardening of gelatin by adsorption processes.

McLaughlin and his collaborators [76] showed that hide substance gets into a reversible equilibrium, as regards Cr and acid, with a chrome salt bath. They found also that the chromium-treated material follows the Freundlich adsorption isotherm. They concluded that chrome tannage is a reversible adsorption reaction. The Freundlich isotherm, however, does not necessarily distinguish between chemical combination and adsorption. In leather tanning and, in a less degree, in gelatin hardening, a colloid chemical factor may become important in advanced stages of the process; but at present this cannot be accepted as an explanation of the fundamental process.

While the interpretation of "basic" and "green" chromium compounds by the co-ordination theory may be unnecessary, it does not follow that the colloid theory must be accepted as the explanation of tanning and photographic hardening.[77,78] Thus, the statement of Crabtree and Russell,[76b] "it may be concluded that the hardening effect of chrome alum is probably a result of the precipitation of chromium hydroxide in the gelatin or at least of a reaction between the basic salt and the gelatin," requires modification. From an examination of the influence of pH upon the apparent viscosity of gelatin solutions and the melting point of the gel in the presence of a chrome salt (introduced in the solution), the following results were established:* The rate of change of viscosity is a function of the pH. At any pH within the range 2–7, in which definite initial increases of viscosity are observed, the viscosity passes through a maximum after a time which depends upon the pH. The increase in viscosity of 7 per cent gelatin and 1.12 per cent chrome alum shows a pronounced maximum at pH 4.03 (Figure 42). The initial viscosity (10 minutes at 40° C. after mixing) itself shows a pronounced maximum at about pH 5.4 (Figure 43). At 1.12 per cent alum, the M.P. gives a maximum at pH ~ 4.8; at 2.0 per cent, at about pH 5.0 (Figure 44). This pH is slightly lower than that at which precipitation is first observed upon titration with alkali (p. 114), *viz.*, 5.3, which corresponds to about 1 equivalent of alkali.

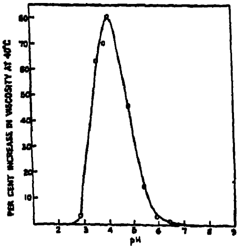

FIG. 42.

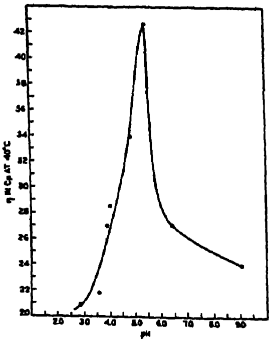

FIG. 43.

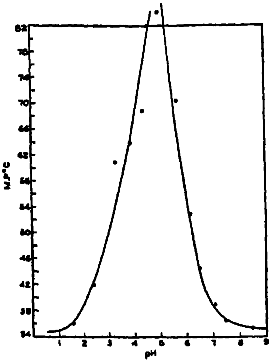

FIG. 44.

FIG. 42. Increase of viscosity with pH for a 7 per cent gelatin solution containing 1.12 per cent chrome alum.

FIG. 43. Relation between the initial viscosity and the pH value of a 7 per cent gelatin containing 1.12 per cent chrome alum at 40° C.

FIG. 44. Relation between the melting point and the pH value for a 7 per cent gelatin containing 1.12 per cent chrome alum.

In accordance with the behavior of aluminum salts, the pH at which chromic oxide starts to separate represents the optimum for hardening. As with aluminum, for hardening from solution (stop baths, fixing baths, and others), this pH is lower (4.3) than when the chrome salt is originally in the solution.

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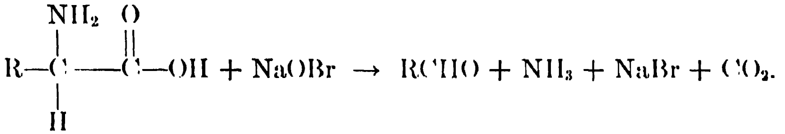
* Unpublished work by R. C. Houck and C. Dittmar in the Kodak Research Laboratories.

The evidence points strongly to the Cr^{+++} ion or $[Cr(H_2O)_6]^{+++}$ being the chief hardening agent, with perhaps to some extent $[Cr(H_2O)_5OH]^{++}$. Hardening increases with pH up to a point because the $—COOH$ groups of the gelatin are increasingly converted to $—COO^-$ ions, and, further, $—NH_3^+$ groups are increasingly converted to $—NH_2$ groups. The evidence indicates that hardening takes place not because of, but in spite of, the increasing precipitation of chromic oxide. The Cr^{+++} ion has the advantage over Al^{+++} that it can form complexes not only with the $—COO^-$ groups of the gelatin but with the $—NH_2$ groups. In agreement with this, the hardening of gelatin by chromium compounds is inhibited not only by polycarboxylic and hydroxycarboxylic acids, such as oxalic, citric and lactic acids, but by amines and amino acids.

The chrome hardening of gelatin is of importance not only in the preparation and processing of emulsions but also indirectly in a wider field. Besides the photochemical hardening of bichromated gelatin and the photographic and photomechanical printing processes derived from it, a number of color-printing processes depend upon chrome hardening. The chrome salt is produced by a direct or indirect reduction of dichromate by the silver of an image.[79] For example, with a copper bleach, the silver is converted to silver halide, which is soluble in thiosulfate, while the cuprous salt reduces dichromate to chromic salt. The hardening of the gelatin may be utilized in the production of relief images, in an altered absorption of dyes, or for transfer procedures.

The hardening of gelatin by halogens is not utilized in photography, but has been suggested as a cause of solarization.[80] It is of interest both in connection with the disposal of halogen released by light and as a link between inorganic and organic hardening. The reactions are probably similar to those involved in the oxidation of amino acids by hypohalites, which have been investigated by Langheld, Dakin, and others.[81] For example, with glycine and sodium hypobromite, the following occur:



$$R-\underset{\displaystyle H}{\overset{\displaystyle NH_2}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH + NaOBr \rightarrow RCHO + NH_3 + NaBr + CO_2.$$

It is supposed that the aldehyde formed produces the hardening. In neutral media, dibromoamino acids tend to form, which decompose and, at higher pH, produce nitriles instead of aldehydes.

HARDENING BY ORGANIC REAGENTS

Above a pH of 6 $\sim$ 6.5, prehardening of emulsions with chromium is ineffective. Organic hardening agents increase in hardening efficiency as the pH is raised above pH 5, approximately the isoelectric point of lime-processed gelatin. This is because, in general, they react with the free amino groups of the protein, and in some cases the original organic reagent is converted to an active form as the pH is raised.

The important organic hardening reagents may be classified as:

1. Aldehydes (aliphatic and aromatic)
2. Ketones (including α- and γ-diketones)
3. Quinones
4. Oxidation products of organic developers of uncertain constitution, which are related probably to synthetic and vegetable tanning agents.

1. Aldehyde Hardening

A. The first of the simple alkyl aldehydes is formaldehyde, $H \cdot CHO$. It is outstanding and is discussed specifically (p. 123). The higher alkyl homologues, if they have sufficient solubility in water to be tested under normal conditions, do not appear to have any hardening effect on gelatin. However, if acetaldehyde, $CH_3 \cdot CHO$, propionaldehyde, $C_2H_5 \cdot CHO$, or butyraldehyde, $C_3H_7 \cdot CHO$, is mixed with an alkaline gelatin (pH 8 and upward) and left in the jelly state for some hours, or if the alkaline solutions in water after keeping are incorporated with gelatin, definite hardening is produced. This acquired hardening is probably due to dimerization and rearrangement to aldols. Thus, with acetaldehyde,

$$2\,CH_3 \cdot CHO \rightarrow CH_3 \cdot CHOH \cdot CH_2 \cdot CHO.$$

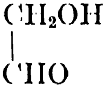
This is supported by the fact that aldol and other hydroxyaldehydes prepared separately produce strong hardening. This dimerization may even occur in formaldehyde hardening with the formation of glycol aldehyde,

$$2(H\cdot CHO) \rightarrow CH_2OH\cdot CHO,$$

which, as noted under hydroxyaldehydes, is an effective hardener.

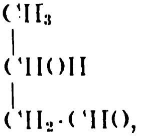
While the pH affects the dimerization of alkyl aldehydes, it is important also directly for the reaction with gelatin. With aldol and glycol aldehyde, for instance, hardening is greatly increased by an increase in pH. This is due to the displacement of the hybrid ion configuration $^-OOC\cdot R\cdot NH_3^+$ to the free amino form, $^-OOC\cdot R\cdot NH_2$, which plays a principal part in aldehyde tanning. As might be judged from the titration curve of gelatin above pH 8, a further increase in pH has little effect until very high values, pH $\sim$ 11, are reached, where it is possible that guanidino residues are opened up.[82]

B. The *hydroxyaldehydes*.* As has already been said, these compounds, of which glycol aldehyde,



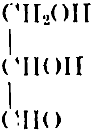
$$\begin{array}{l} CH_2OH \\ | \\ CHO \end{array},$$

aldol,



$$\begin{array}{l} CH_3 \\ | \\ CHOH \\ | \\ CH_2\cdot CHO, \end{array}$$

and glyceric aldehyde,[83]



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CHO \end{array},$$

are examples, are effective hardeners of gelatin at pH 8 and above. The M.P. measured immediately after coating and drying increases rapidly with the concentration of aldehyde. It is increased by holding in the jelly state and also by keeping in the dry state (after hardening). Thus, with 3 per cent of aldol (by weight of gelatin), after seven days gelatin becomes insoluble in boiling water; and with 1.3 per cent of glycol aldehyde, after sixteen days. The viscosity (at 40° C.) of gelatin solutions with these materials increases somewhat but not to the degree produced by chrome salts.

Photographically, aldol and glyceric aldehyde tend to cause fog. In the case of aldol, this may occur from loss of water and the production of crotonaldehyde,

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* From unpublished experiments in the Kodak Research Laboratories.

$$CH_3 \cdot CHOH \cdot CH_2 \cdot CHO \rightarrow CH_3 \cdot CH : CH \cdot CHO + H_2O,$$

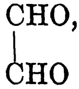
and with glyceric aldehyde, from the production of the enolic form of methylglyoxal,

$$CH_2OH \cdot CHOH \cdot CHO \rightarrow CH_2 : C(OH) \cdot CHO + H_2O.$$

As noted later, the unsaturated aldehydes are strong fogging agents.

These hydroxyaldehydes are interesting since they show the activation of the —CHO group in the hardening reaction which is produced by substitution of hydroxyl. This effect extends to the pentoses and hexoses.[84] With this extension of chain length, there is a diminishing rate of hardening, which may be raised by increasing the temperature.

C. The *dialdehydes.* The activating influence of hydroxyl substitution is paralleled by that of other substituents, notably the —CHO group itself. The dialdehydes have effective hardening action.[85] Principally cited are glyoxal, $\begin{array}{l}\mathrm{CHO}\\ |\\ \mathrm{CHO}\end{array}$, its polymer, *p*-glyoxal, and mesoxydialdehyde.



D. The unsaturated *aliphatic aldehydes.* Unsaturation, as by a double bond near the —CHO group, has a considerable activating effect on the hardening action of the aldehyde group, as in acrylic aldehyde (acrolein)

$$\begin{array}{rll} & CH_2 : CH \cdot CHO & \text{acrolein} \\ \text{and} & CH_3 \cdot CH : CH \cdot CHO & \text{crotonaldehyde.} \end{array}$$

These substances tend to produce fog, a common feature of unsaturated bodies of this type, probably due to the formation of peroxides.

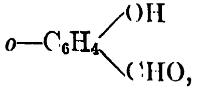
It is interesting that the substitution of halogen in aliphatic aldehydes also acts as an activating factor. Dibromacrolein, $CH_2Br \cdot CHBr \cdot CHO$, is patented[86] as a hardening agent, and there is other evidence of activation by halogens.

E. Carboxylic aldehydes. Mucochloric acid,[87]

$$CHO \cdot ClC : CCl \cdot COOH,$$

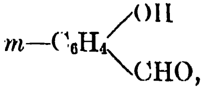
is a fairly powerful hardening agent, in which the activating effect of substituted groups is well developed. The application of other aliphatic aldehyde carboxylic acids has been claimed.[88]

F. Aromatic aldehydes. Aromatic aldehydes, corresponding to the quasi-unsaturated character of the benzene nucleus, show some tendency to produce hardening. Benzaldehyde appears inactive at room temperature. Salicylaldehyde,



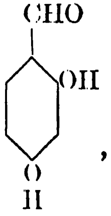
$$o\text{—}C_6H_4\begin{array}{l}\diagup OH\\ \diagdown CHO,\end{array}$$

gives hardening in the jelly state, as does the meta compound,



$$m\text{—}C_6H_4\begin{array}{l}\diagup OH\\ \diagdown CHO,\end{array}$$

while resorcylic aldehyde,

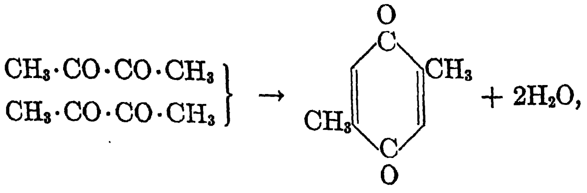


has definite hardening properties at pH 8. It also increases the hardening action of formaldehyde (v. later).

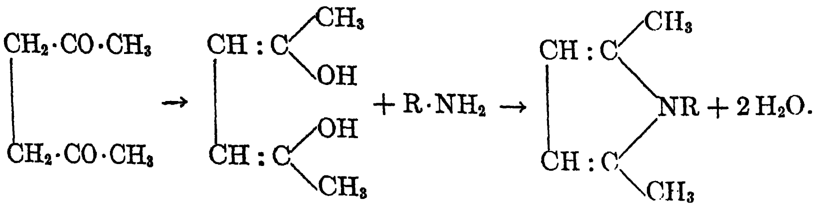
2. Ketones

Aliphatic hydroxyketones, including ketones of the sugar group, have been claimed as hardeners for proteins.[89] The hardening effect is stated to decrease with the number of carbon atoms and to increase with the number of hydroxyl groups. As examples, are instanced acetol ($CH_3CO\cdot CH_2OH$), dihydroxyacetone ($CH_2OH\cdot CO\cdot CH_2OH$), 3-ketobutanol-1, hydroxymethylene acetone, fructose, and sorbinose. Certain hydroxy aromatic ketones, such as *p*-hydroxybenzoyl carbinol and 2,4,6-hydroxybenzoyl carbinol, are also stated to have hardening properties.

Of greater activity and importance are diketones, *viz.*, α- and γ-diketones; so far, there is no evidence that β-diketones have hardening properties. A typical α-diketone with considerable hardening properties is diacetyl,[90] $CH_3\cdot CO\text{—}CO\cdot CH_3$. Its action, which occurs on the alkaline side (pH > 7), is probably due to the formation of xyloquinone. In the alkaline medium, two molecules condense,[91] with the loss of two molecules of water,

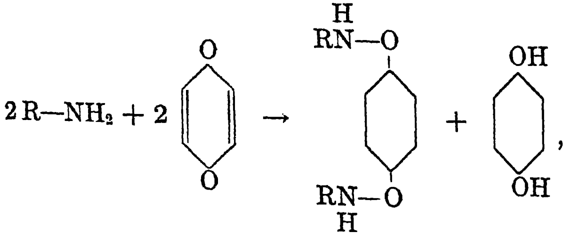


and form xyloquinone. The chemistry of the hardening action of diacetyl, therefore, belongs with that of the quinones. The production of the quinone can be followed by ultraviolet absorption spectroscopy. The hardening of gelatin is also effected by γ- or 1 : 4-diketones; for example, acetonyl acetone, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$. The chemistry of the reaction has not been fully explored, but it is possible that, by a reaction similar to that with ammonia, a combination with amino groups occurs to form pyrrole derivatives, the ketone reacting in the enol form:



3 and 4. Quinones and Developer Oxidation Products

Hardening by benzoquinone was first noted by Lumière.[92] It is markedly dependent upon pH, being very slight at pH ~ 5.0 and negligible below that.* Above pH 5, it increases rapidly at first and more slowly from pH 8 upward. Photographically, it is of little use because of the red stain formed by oxidation reactions. The hardening or tanning reaction is said to result from interaction of the quinone with free amino groups,[94] as



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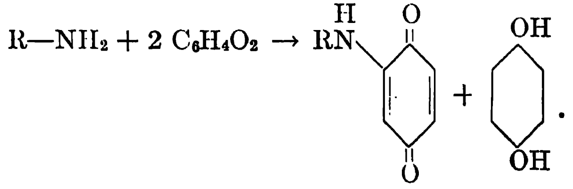
* Observed by Meunier and Seyewetz with collagen [93] and confirmed for gelatin by R. C. Houck and C. Dittmar of the Kodak Research Laboratories.

or, according to Hilpert and Brauns,[95]



But beyond the evidence of formation of hydroquinone, there is little to support this result.

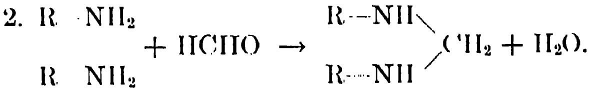
While reactions of the type indicated above may take place, more complicated stages probably supervene, similar to those involved in the hardening of gelatin by developer oxidation products. It is probable that a quinonoid body is the primary oxidation product of organic developers and that it is this which reacts with gelatin and produces hardening. Both staining and tanning by developers are lessened or eliminated by sulfite, which interacts with quinones to form sulfonic acids of the reducer (Chapter X).

This hardening in development, to a degree depending upon the amount of silver reduced, has been applied in various washoff relief and imbibition processes ever since it was patented by Warnerke.[96]

Formaldehyde

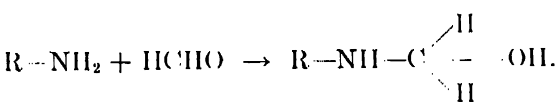
Formaldehyde holds a position among organic hardeners similar to that of chrome salt among the inorganic; at least, it has received the most attention. Comparative studies of the reactions of formaldehyde with amines and amino acids have been applied to clarify the reaction with proteins. Blum [97] suggested that formaldehyde might condense with one or two molecules of an amine and produce methylene groups according to the scheme:

1. $R—NH_2 + HCHO \rightarrow R—N{=}CH_2 + H_2O$,



2. $$\begin{matrix} R—NH_2 \\ R—NH_2 \end{matrix} + HCHO \rightarrow \begin{matrix} R—NH \\ R—NH \end{matrix}\!\!>CH_2 + H_2O.$$

Benedicenti [98] suggested an intermediate addition phase,



$$R—NH_2 + HCHO \rightarrow R—NH—C\begin{matrix} H \\ — OH \\ H \end{matrix}.$$

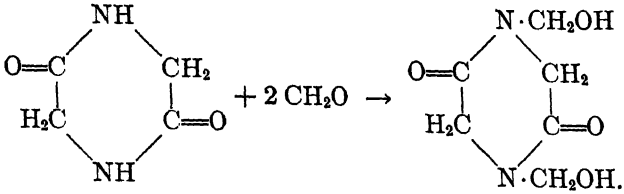
Schiff [99] and Sorensen [100] showed that after the addition of formaldehyde to amino acids and proteins, the carboxyl could be titrated directly, with the formation of methylene groups:

$$NH_2—R—COOH + HCHO \rightarrow H_2C=N—R—COOH + H_2O.$$

The analytical use of this was developed more fully by Foreman.[101] An early quantitative study of the action of formaldehyde on gelatin and collagen was made by Lumière and Seyewetz.[102] They found that if a 10 per cent aqueous solution was allowed to act upon air-dry gelatin, the maximum amount fixed was between 4.0 and 4.8 per cent. The insoluble "formo-gelatin" was decomposed by repeated treatment with boiling water or cold 15 per cent hydrochloric acid. However, the amount of formaldehyde "fixed" by gelatin, as by other proteins, is a quantity depending not only upon the conditions of reaction but on the criterion of "fixation." According to the Schiff-Sorensen reaction, whatever the mechanism,[103] only amino groups of the diamino acids would be available, and at pH > 9, only those of lysine, a triamino acid. This would permit the "fixation" of only about 1.23 gms. of formaldehyde per 100 gms. of gelatin. Einhorn [104] found that acid amides combine with formaldehyde, thus:

$$R \cdot CONH_2 + CH_2O \rightarrow R \cdot CO \cdot NH \cdot CH_2OH.$$

But the amount of amide-N in lime-processed gelatin, as shown by the yield of ammonia with alkali, is very small.* Cherbuliez and Feer [105] observed a similar type of reaction with diketopiperazine:



This reaction was confirmed by Bergmann,[106] who also isolated triformal derivatives of glycine ethyl ester, glycine amide, and γ-amino-propylene-glycol. These results at least show the possibility of the formation of higher order compounds of formaldehyde with proteins. Also, it should be noted that, if an aqueous solution of formaldehyde is evaporated, it will leave a residue of insoluble polymerized formaldehyde (polyoxymethylene). That a certain amount of this may be formed upon drying formaldehyde gelatin is possible.

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* Acid-type gelatin has a much larger amount of amide-N, but the reaction with formaldehyde has not been investigated thoroughly.

Brotman [107] found that while dry gelatin absorbs 0.98 gm. of formaldehyde per 100 gms. of gelatin, a 10 per cent jelly absorbs 1.12 gms., and a 5 per cent jelly, 2.12 gms. These figures were based on the formaldehyde removed from a solution and apparently did not take account of the solution absorbed.

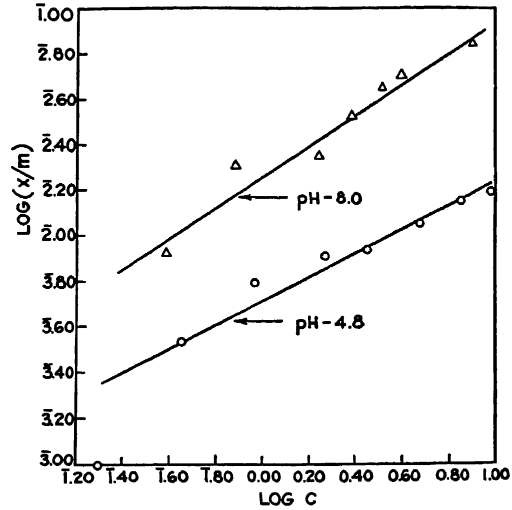

FIG. 45. The absorption of formaldehyde by gelatin.

The following results were obtained * for the absorption of formaldehyde from an alcoholic solution, which did not change the swelling appreciably: Five grams of gelatin were dissolved at pH 8 in 25 cc. of water and 200 cc. of formaldehyde solution added at various concentrations. The precipitated gelatin was soaked at 4° C. for six days and then repeatedly washed with 50 per cent alcohol. Analyses of solution and washings gave the final concentration of unabsorbed formaldehyde solution, while the hardened gelatin was steam-distilled to determine the absorbed formaldehyde solution. Another series was run

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* Unpublished work by H. R. Brigham of the Kodak Research Laboratories.

at pH 4.8. Figure 45 gives graphs for these results plotted logarithmically in terms of the Freundlich adsorption isotherm $\log x/m = k \log c + p$.

The "fixation" curves correspond to the Freundlich adsorption isotherm. This does not exclude chemical combination to some extent but indicates that there is also physical or mechanical retention.

There is a further interesting parallel between the hardening of gelatin by chrome salt and formaldehyde. In both cases, fairly simple chemical reactions can be postulated for an initial stage; but combination proceeds further, and the over-all take-up is representable by an adsorption isotherm. In the advanced phases, condensation products of higher order are produced, and there is probably also some retention of the polymerized reagent.

Even in the case of amino acids, there is evidence that relatively complex bodies are formed with formaldehyde. An investigation of the X-ray diffraction patterns[108] of amino acids treated with formaldehyde showed that while the histidine-formaldehyde product is highly crystalline, the derivatives of lysine and arginine are amorphous. It appears probable that a condensation or polymerization takes place, the formaldehyde serving as a cross linkage between the amino groups of the diamino acids (p. 123). There is some evidence that formaldehyde in small amounts acts catalytically on the insolubilization of gelatin, and this may be connected with the production of insolubilization by heat. All hardening by aldehyde is greatly accelerated by rise of temperature.

A phase of formaldehyde hardening of gelatin which may approach the tanning of hide by so-called "syntans"[109] is indicated by the discovery of the assisting action of phenols and phenolic aldehydes[110] upon aldehyde hardening, particularly with formaldehyde. There may be some formation of aldehyde-phenol condensation products. This is supported by the existence of an optimum concentration of the phenolic compound.[111]

The chemical reactions for the action of hardeners suggested in this chapter should be considered as tentative. In any case, the hardening of gelatin is probably accomplished by the establishment of cross linkages.

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PART II

THE ACTION OF LIGHT

CHAPTER IV

THE SENSITIVITY OF THE SILVER HALIDE GRAINS AND THEIR RESPONSE TO LIGHT

The light-sensitive photographic emulsion, as discussed in the previous chapters, consists of an assemblage of flat triangular or hexagonal grains of silver bromide suspended in gelatin. Adsorbed to the grains are gelatin itself and, by implication, some of the components of gelatin and other substances, such as alkali halides available during the preparation of the grains.

If the photographic emulsion is immersed in a suitable reducing solution, known in photography as a *developer*, no change occurs for a considerable time provided that the emulsion has not been exposed to light; but if an exposure to a very small amount of light has been given, the grains are transformed into masses of metallic silver, the bromine going into solution as alkali bromide. If the silver bromide has been exposed to a very large amount of light, it is decomposed to a considerable extent, contains free metallic silver, and gives up bromine to the gelatin or the atmosphere. Exposure to a considerable amount of light, therefore, produces a visible image; and, by analogy, the change which occurs in the silver bromide by exposure to small amounts of light, as a result of which it becomes developable, is termed in photography the *latent image*.

The study of the action of light on the emulsion involves (1) the special structure of the individual grains by which the absorption of a very small amount of light renders them developable, (2) the immediate effect of this small amount, that is, the nature of the latent image in the grains, and (3) the distribution of the exposed grains throughout the thickness of the emulsion and, thus, the relation of the number and distribution of the developable grains to the exposure to light which made them developable.

Early studies of the development of silver bromide grains showed that development of a grain continues until all the silver bromide has been converted into metallic silver. The initiation of development depends upon the exposure; strongly exposed grains start to develop more rapidly than those with less exposure, but once development commences in a grain it goes to completion if the supply of developer is sufficient. Moreover, there is normally little transference of silver bromide in solution from one grain to another, that is, the silver which forms a grain in the finished image is derived chiefly from the grain of silver bromide in that place and not from other grains nearby. The silver bromide grains tend to stick together in clumps, however, two or three small grains attaching to each other; and if one of these grains is affected by light, the whole clump becomes developable. The developability of a clump by infection from a single exposed grain has been questioned. The subject is discussed in Chapter XXI, p. 832.[1,2]

In a study of the action of light upon silver halide grains, it is necessary, first, to reach a conclusion as to the nature of the latent image, then to deal with its distribution on the grains, the relation of the sensitivity of the grains to their structure, the primary photochemical reaction involved, and the mechanism by which the latent image is formed.

THE NATURE OF THE LATENT IMAGE

Bancroft[3] was one of the first to correlate the information concerning the invisible image. In a series of papers, he presented, by selecting and translating from the voluminous writings of Carey Lea, Lüppo-Cramer, Eder, and others, records of fact and opinion on the latent-image problem as it was known before 1910. In 1923, he reviewed later work in an address before the Faraday Society.[4]

The general question at issue is: *What happens to an emulsion grain when it is altered by light?* The amount of work required to alter a really sensitive grain is very small, and the change brought about by so little energy is likely to be small. This led Bose[5] to suggest that the grains acquired a vibratory strain, analogous to that supposed to exist in plants and animal tissue after stress, which would raise the grains to a higher energy level and enable them to react with the developer.

Namias,[6] Hurter and Driffield,[7] and Chapman Jones[8] assumed some change of state involving, perhaps, polymerization, de-polymerization, or conversion to a metastable variety. Bredig[9] put forward a disintegration theory, according to which a number of very small granules would result from a parent grain. It was thought that their increased solution pressure would be sufficient to start development.*

The idea that the effect of light is to produce only a physical alteration of the silver halide has long been abandoned because of the well-defined chemical reactions other than development which characterize the latent image. Certain chemical substances can duplicate the action of light by producing developability, and most of them are *reducing agents*. Others can destroy the latent image and destroy sensitivity to light, and they are *oxidizing agents*. It has, therefore, been accepted for many years that the action of light on a silver halide is one of reduction. Thus, H. B. Baker, in 1892, demonstrated the expulsion of some chlorine from silver chloride by light; and the separation was proved beyond doubt by Hartung,[10] who weighed deposits of silver halides on very light supports suspended in a microbalance. His instrument would carry a load of 125 mg. and was sensitive to 2×10^{-5} mg. The silver was deposited on quartz, carefully chlorinated or brominated with free halogen, and exposed in a relatively high vacuum for some days to strong sunlight. A complete removal of halogen was never effected, and the quantity remaining varied with the nature of the residual gas in the apparatus. The maximum percentage loss of chlorine, no matter how long the exposure to light, was 91 per cent for air, 89.9 per cent for nitrogen, and 94.8 per cent for hydrogen.

From these experiments, it is clear that the product of the prolonged action of light on silver chloride or silver bromide is either metallic silver or some form of subhalide. The idea that the reduction product is subhalide was proposed by Carey Lea as the result of his prolonged researches[11] on the photohalides undertaken long before photographic science was ready to use them. He believed that the latent image was formed of silver subhalide dispersed colloidally in unchanged normal halide. He had noticed that silver halide precipitated in the presence of dyes carried down quantities of the latter, which were held very firmly and rendered much more stable to fading and chemical action than they would be alone. By analogy, he supposed the latent-image material to be subhalide imprisoned or *adsorbed* by the normal salt. He clung to the subhalide theory because he could not believe that, even if there were sufficient energy in the light to produce free metal, the occluded metallic silver could resist the attack of solvent. It is known, however, that small quantities of adsorbed substances have properties quite different from those which the substances exhibit in bulk or if they are out of contact with an adsorbing surface. Lea was able by chemical means to produce a number of silver halides containing less halogen than the normal salts. They were highly colored owing to the presence of reduced material in a dispersed condition. He named them *photohalides* because they could also be made by the printing-out action of light. According to Lea, photohalides

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* These suggestions are of historic interest only, and in the light of present knowledge do not demand serious attention.

> "*are obtained in an endless variety of ways:* by chlorizing metallic silver; by acting on normal chloride with reducing agents; by partly reducing silver oxide or carbonate by heat and treating with hydrochloric acid; by forming sub-oxide or sub-salt of silver and treating with HCl followed by nitric acid; by acting on subchloride * with nitric acid or an alkaline hypochlorite."

Light, therefore, did not form a pure photosalt. Carey Lea called *photosalts* those colored halides containing reduced material which were not further altered by concentrated nitric acid. It is probable that the action of acid in the preparations mentioned above was merely to remove reduced silver situated very near the surface. Lea himself remarked that prolonged boiling destroys even the photohalides; about twenty-five hours were required to banish the color from the red chloride in nitric acid of sp. gr. 1.35. On complete analysis, the photosalt yielded reduced material, which he expressed as

Subchloride	2.49 per cent
Normal chloride	97.51 per cent.

This could have been interpreted equally well as

Silver	2.14 per cent
Normal chloride	97.86 per cent

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* Produced in bulk from the subfluoride after the manner of Guntz by treating a soluble silver salt with a reducing agent.

and would have required no assumptions regarding a subcompound, the existence of which could not be substantiated in any other way.

In the last twenty years, views of chemists as to the nature of substances such as photosalts have been modified very greatly. It is realized that in solids, such as silver bromide, it is possible for considerable quantities of free metallic atoms to be present and that these cause a strong color in the crystal; rock salt, for instance, can be colored to a deep blue by the presence of free sodium.

The subhalide theory attracted a great deal of attention from photographic workers and was endorsed by many authorities. It was given considerable support by the work of Guntz,[12] who definitely isolated the subfluoride, Ag_2F, the formation and structure of which were confirmed and elucidated subsequently. But Guntz was unable to prove the existence of the other subhalides, for which, indeed, the energetic and chemical factors permitting the formation of the subfluoride do not obtain. This led to a series of complete investigations by Luther,[13] Baur,[14] and others with a view to proving electrochemically that a subchloride of silver can exist. Luther's method was to measure the potential difference between suspensions of silver chloride and suspensions of silver progressively oxidized by chlorine. This work represented the last serious support for the subhalide theory of the latent image, since the application of X-ray spectral analysis has placed beyond doubt the nature of the product of the prolonged exposure of silver bromide to light.

In 1925, Koch and Vogler [15] showed that if silver bromide is exposed to light, its X-ray powder spectrum, using the Debye and Scherrer method, shows lines characteristic of metallic silver. Moreover, if the exposed silver bromide is fixed with thiosulfate, the remaining material shows only the silver lattice. This was confirmed by Trillat,[16] who found that if a film was exposed for ten days to ordinary light and was then fixed in thiosulfate, the X-ray spectrum showed distinctly the rings corresponding to aggregates of silver and that, as exposure was continued for weeks or even months, the amount of silver grew. In the case of a film exposed for several months to daylight but not fixed, the spectrum showed the presence of both the silver bromide and metallic silver. No trace of silver could be found in films which had not been exposed for a long time; that is, these observations give no direct evidence as to the nature of the latent image, but they prove beyond doubt that prolonged exposure to light produces metallic silver from silver halides.

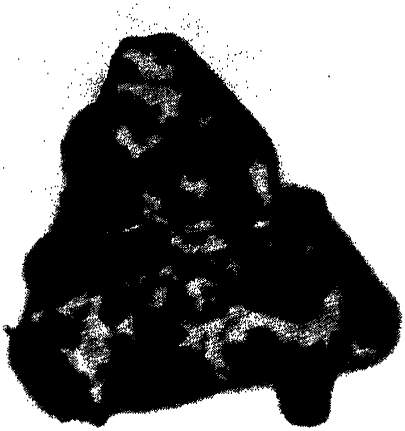

FIG. 46. Electron microscope photograph of a silver bromide crystal exposed to intense electron beam. ×36,000.

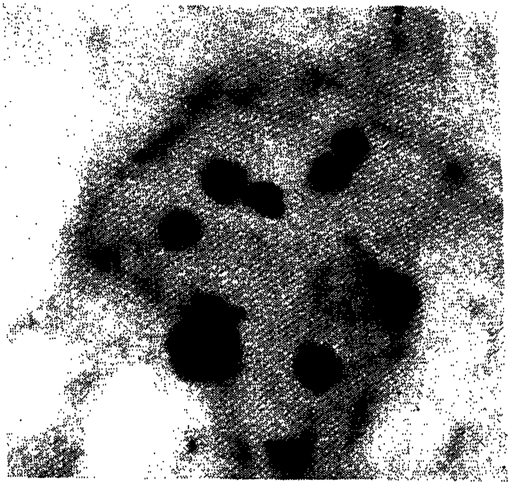

FIG. 47. Electron microscope photograph of photolytic silver particles (silver bromide exposed to ultraviolet light, fixed). ×50,000.

The electron microscope makes it possible to carry the study a little further. Thus, Figure 46 shows a crystal of silver bromide after exposure to the beam in the electron microscope. Black deposits have been formed in the crystal, which is breaking down under the electron beam. Figure 47 shows a silver bromide crystal which has been exposed to strong light and then fixed. A shadow of the original crystal in the gelatin is seen and also a large number of small specks of metallic silver remaining after the fixation, of which the smallest are estimated to be less than 200 A across. These small units appear to be cubical crystals of silver, in which case they would have about 2500 atoms of silver in a face, or a total content of 125,000 atoms.

In view of the continuity between the formation of the latent image and the production of a visible image, there seems to be every reason to believe that the latent image produced by exposure to light consists of aggregates of metallic silver.

As an alternative to the view that the latent image is formed by the liberation of silver atoms from the silver halide, Renwick suggested that preformed silver particles are changed by light from a *sol* to a *gel* form, and in this way nuclei for development are obtained. Furthermore, Weigert [18] built up a micelle theory of the latent image from his experiments on induced optical anisotropy, according to which the latent image must be formed from physically changed micelles—dense, yet amorphous aggregates of molecules of all constituents of the emulsion: the original silver, dye, silver sulfide, and the silver halide itself. The change upon exposure to light, which represents a spatial orientation of the micelle elements, corresponds simultaneously to an increased catalytic activity toward the developer.

The fact that the photochemical decomposition of silver halide crystals is oriented was shown by Trivelli and Sheppard.[17] In crystals prepared from ammonia solution, the decomposition developed along certain definite directions; but in emulsion grains it occurred at points scattered more or less at random on the grain surface.

The strongest argument that the *normal* latent image, in the absence of optical sensitizers, is produced from silver halide itself is furnished by the spectral absorption factor. The spectral sensitivity curves of the silver halides agree, about as well as could be expected, with the *apparent* spectral absorption curves of the silver halides—apparent, because the determination of true absorptions for dispersed light-scattering materials is far from easy. But it appears that the spectral sensitivities of silver chloride, bromide, and iodide are determined by the halide, a fact borne out by the behavior of mixtures, whereas according to Weigert's hypothesis they should be determined, without reference to the halogen, only by the specific silver-adsorption complex or *sensitivity speck.* In confirmation of this, desensitizing by chromic acid and other oxidizers does not change the relative spectral sensitivity distribution, although it reduces its absolute value greatly (p. 159).

THE DEVELOPMENT CENTERS

The mass of the latent image which can initiate development is so small that its chemical nature cannot be identified by direct analysis; but in view of the evidence that the prolonged action of light on silver bromide produces metallic silver and that this occurs in the form of definite specks on the surface of the grain, as shown by the microscope, it is reasonable to assume that the latent image also consists of metallic silver and that this silver is located in patches rather than disseminated through the mass of the grain. These patches of silver may be considered to form developable centers.

In 1917, Hodgson,[19] following some tentative experiments made by Scheffer in 1907,[20] noticed that if development were interrupted just before the appearance of an image and the grains were examined microscopically, black specks were visible in or on the grain, appearing larger and greater in number the longer the time elapsing before inspection; they were evidently centers of silver deposition.

The investigation of the nature and occurrence of the centers was undertaken by a statistical method. Three groups of workers became interested in the problem at about the same time—Svedberg and his associates at Uppsala, the British Photographic Research Association in London, and the Kodak Research Laboratories in Rochester, New York. Inasmuch as a single grain which contains a development center becomes completely developable, the effect of exposure in increasing the density must be due to an increase in the number of grains in which are produced development centers; that is to say, the probability of a grain becoming developable depends upon the exposure. According to this view, the greater sensitivity of larger grains (see p. 146) arises from the greater probability of their producing a developable center during exposure.

The distribution of the centers among the grains was studied by Svedberg (Chapter V, p. 212) and found to follow Poisson's law of chance distribution, according to which the percentage probability for the occurrence of n centers in a grain is

$$P_n = \frac{100 \cdot e^{-v} \cdot v^n}{n!},$$

where v is the average number of centers per grain. Thus, the percentage probability that the grain contains at least one center is

$$P = 100(1 - e^{-v}).$$

The haphazard distribution of the centers explains the fact that not all the grains of a certain size are made developable by a certain exposure. Svedberg made experiments the results of which agreed so closely with the theory that he concluded that there was little doubt that the centers were really distributed according to the laws of chance. He prepared plates on which were coated a large number of grains in single layers. These were then developed for a short time in order that the centers might be developed, and photomicrographs were made to obtain a record of the grains and of the number of centers in the different grains.[21] The negatives were printed by projection, so that the image of each grain would fit closely into the same circular area; that is, all of them were made the same size even though this required varying degrees of enlargement. The prints were superimposed by turn on a piece of drawing paper and the positions of the centers pricked through. In this way, a composite record was obtained of the likely positions in a large number of grains. The 244 centers in the experiment fell within a circle of a certain diameter. Another circle of half the diameter was drawn concentrically, and the number of centers occurring in the inner circle and the outer annulus were counted separately. The ratio of the two numbers was found to be 1 : 6.6.

It is easy to calculate the theoretical ratio if the centers inhabit the surface only and to show that it is different from the value deduced when they are dispersed throughout the volume. In the first case, it is

$$\frac{\sqrt{3}}{2 - \sqrt{3}} = 6.5,$$

while in the second it is

$$\frac{\sqrt{3}}{8/3 - \sqrt{3}}, \text{ or } 1.9.$$

The experimental value of 6.6 points emphatically to surface distribution. It may be accepted, therefore, that the centers at which development starts are situated on the surface of the grains in haphazard distribution. If the silver halide material is homogeneous, the probability that a center will form should be proportional to the area of the grain. High-speed emulsions contain flat tablets, which generally lie parallel to the surface of the film; and the projective area is closely related to the total area.

Svedberg found that in his emulsions the probability of occurrence and the projective area were nearly proportional for the various grain classes. He defined the specific sensitivity of the grains as the *average number of developable centers per square centimeter of surface of silver halide in any given emulsion resulting from unit exposure to light.* The specific sensitivity was found to differ widely from one emulsion to another. Svedberg's definition of sensitivity stated in unequivocal language the well-appreciated fact that large grains are more sensitive than small ones and are more likely to develop centers.

Toy [22] investigated the specific sensitivity of four classes of grains in a single layer of a very uniform emulsion. By counting the number of grains rendered developable in each class for each exposure, he was able to construct characteristic curves for each class which resembled the $D \log E$ curve of a multilayer plate (Chapter V). If his emulsion grains were separated into four classes, the curves reproduced in Figure 48 were obtained. The larger grains proved more sensitive and more similar to one another than the smaller.

The evidence that development started from definite centers on the silver halide grains led to an important discussion of their origin. They were clearly associated in some way with the manner in which light acted, and three possibilities presented themselves:

1. The development centers might be due to the incidence of heterogeneous radiation on homogeneous crystal surfaces.

2. They might exist in the grain before exposure and differ from the rest of the silver bromide, the incident light being uniform and not necessarily discrete in structure.

3. By a combination of 1 and 2, they might be the result of discrete radiation incident on heterogeneous crystal surfaces.

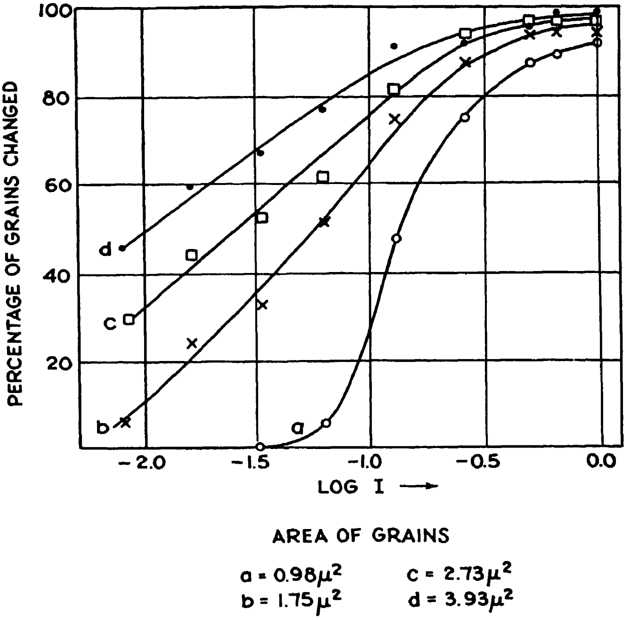

Fig. 48. The relation between the area of grains and their sensitivity to light.

A fourth possibility, that development had to start *somewhere* and that it started at points, was soon discounted as responsible for the existence of the centers, for, if this were the case, they would grow in number as the time of development increased; but in practice this does not occur.

The first hypothesis mentioned above was put forward by Silberstein [23] as the "light dart" theory, based on the quantum theory of radiation (Chapter V). Later, Silberstein [24] modified his theory to bring it into line with the third possibility. Toy's [25] experimental work supported the conclusion that a material other than silver bromide was distributed at points on the grain surfaces, and he assumed that it was present in the form of separate particles produced during precipitation and ripening. For any normal exposure, it is these particles which provide the reduction nuclei, the only function of exposure being to change their condition so that they become susceptible to the action of the developer. All nuclei do not require the same intensity to change them; they are distributed among the grains according to the laws of chance; only grains which have at least one nucleus are developable, and the average sensitivity increases with the size of the grain. The sensitivity of a grain is that of its most sensitive nucleus. This was the hypothesis adopted by Toy,[22] on which he based an extensive series of investigations which lent support to it.

Svedberg had assumed a similarity between the light-sensitive material in the large and small grains, but considered the sensitivity of a nucleus to be independent of the size of the grains, so that the only effect of increasing the size would be to increase the total number of nuclei. More recent evidence is that the sensitivity specks themselves are not the light-sensitive substance. The possibility that the sensitivity might be increased by traces of material not silver bromide led to the proposal that this material might be affected by chemical reagents which would not attack silver bromide and thus the action of light could be simulated by chemical means.

In this way, light was shed on the nature of the centers by investigators, notably Clark, who studied their production by chemical fogging agents. It had been observed as early as 1887 [26] that an emulsion could be made developable by chemical agency in the absence of light, even to the production of reversal.[27] Perley [28] in 1909 showed that hypophosphites, arsenites, and stannous salts fogged emulsions; and his findings were corroborated by Bancroft.[29] Clark,[30] in the first of a series of papers concerning the fogging action of arsenites and hydrogen peroxide, suggested that the pre-existence of sensitivity centers in the emulsion grain could be proved if chemical reagents affected the grains quantitatively and statistically in the same manner as light. Furthermore, if chemical action duplicated light action, the vexed question of separate light quanta versus continuous wave reception might be irrelevant to the photographic effects. For his experiments, Clark used single-layer plates coated with an emulsion of the kind used by Toy, in which the grains were flat tablets, all of much the same shape and size.

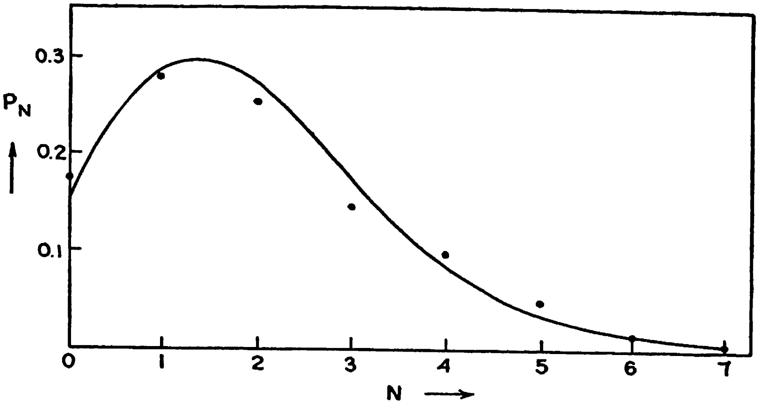

FIG. 49. The production of developability by treatment with sodium arsenite.

Toy had verified Svedberg's conclusion that the likelihood of n centers being found in an exposed and partially developed grain could be denoted by

$$P_n = \frac{e^{-v} \cdot v^n}{n!},$$

where v is the average number of centers per grain. Clark obtained a curve connecting n with P_n for plates treated with 10 per cent sodium arsenite, which exactly duplicated the curve obtained from light action (Figure 49). He found, furthermore, that the arsenite centers were situated in the same regions on the grains as the light-activated centers. The ratio of the number of centers on the flat portions of the grains to the number on the edges was 1 : 2.3 in each case. The actions of light and arsenite appeared identical.

To obtain heavy fogging, Clark had employed solutions containing as much as 10 per cent of commercial sodium arsenite.

To insure that this fog did not result from interaction between the arsenite and the silver bromide but from the reaction of arsenite on the sensitivity centers, he compared [31] the action of the arsenite solution on an untreated plate with that on a plate from which the sensitivity centers had been removed by oxidation. The developability in the second case appeared negligible compared with that in the first. Clark also [32] investigated the formation of complexes between silver salts and arsenite solutions. In the case of mono-sodium arsenite solution, no reaction was found, but there was a very pronounced reaction upon the addition of more alkali. Sheppard, Wightman, and Trivelli,[33] who investigated the attack of arsenite solutions on silver bromide, found a very rapid reduction to silver in the case of the di-sodium arsenite. They even found a slight reduction with mono-sodium arsenite when silver bromide was agitated with the solution for a long time.

The fact that oxidizing agents can destroy the latent image is an important point in the theory of nuclei. Joly [34] in 1905 had shown that uranyl nitrate reduced sensitivity, and Lüppo-Cramer [35] had noticed the effect of chromic acid in depressing sensitivity when it was added to the liquid emulsion during manufacture. Abney, Schaum, Lumière, Reiss, and many others had reported the action of such salts as cupric sulfate and mercuric chloride. A very thorough survey of the action of oxidizing agents, in particular of chromic acid, was made by Eder.[36] Bullock assembled most of the published data concerning the chemical reactions of the latent image in a monograph, which includes much of his own work. The book contains an extensive bibliography, and the reader is referred to this for detailed information.[37]

Sheppard and Mees [38] investigated quantitatively the action of chromic acid on sensitivity, development, and the destruction of the latent image. They showed that both γ and speed are greatly reduced by immersion, after exposure, in $N/50$ chromic acid solution.

Clark [32,39] studied the action of chromic acid on silver bromide before and after exposure to light. He plotted curves showing the increase in the percentage number of grains changed with the increase in exposure for single-layer plates which had received treatment before exposure. Curve A, reproduced in Figure 50, is from the original emulsion, while curves B_2 and B_3 are from measurements on plates which had received short and long desensitization in chromic acid. Essentially, chromic acid moves the curves to the right along the exposure axis, indicating a reduction of speed. The effect of the desensitizer was most marked on the smaller grains, as had been noticed by Sheppard.[40] This is shown plainly in Table VII, compiled from Clark's data:

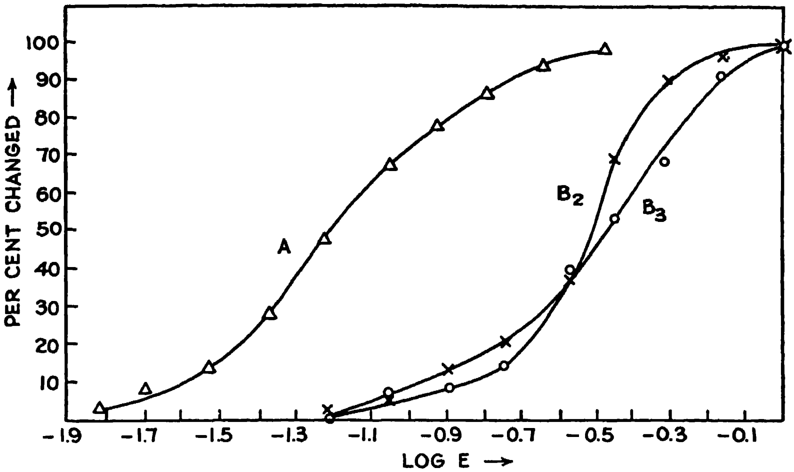

FIG. 50. Developability of silver halide grains treated with chromic acid.

TABLE VII

Grain Area in μ^2	*Percentage Number of Grains Changed* *Desensitized*	*Untreated*	*Ratio*
4.9	67.9	100.0	1.47
2.4	55.0	85.0	1.55
1.76	42.0	75.0	1.78
1.23	17.9	52.3	2.92

These results are plotted in Figure 51.

One of Clark's most interesting experiments concerned the action of chromic acid on ordinary commercial (not single-layer) plates previously exposed to light. Because developability after exposure is destroyed by chromic acid, the plate can be exposed again and will record a new image. Clark found that the reduction in speed by this desensitization was much greater for plates which had received pre-exposure than for those which had not. The desensitization was almost independent of the time of immersion in the chromic acid and differed in this respect from the plates which had not received pre-exposure (Figure 52). The depressing effect of pre-exposure became less marked the slower the emulsion, until, with a slow-process plate, exposed or unexposed, the curves were identical (Chapter VII, p. 295).

From these experiments, some deductions can be made concerning the sensitivity substance. It would appear to be less attackable than the latent-image substance, as after light exposure it becomes reactive and completely removable. The inference might be that light changes the sensitivity substance into the latent-image substance, but this explanation is not entirely adequate because with very slow plates the action of the oxidizer is the same with and without exposure. It is sufficient to state, therefore, that the sensitivity substance is possibly more plentiful, but certainly more resistant, in the large and fast grains. The ratio of the numbers of development centers on the edges of the grains to those on the flat surfaces was found by Clark to be reduced from 2.3 : 1 to 1.05 : 1 after exposure and desensitization. This again supports the view that a special sensitivity substance had been removed from the edges of the grains.

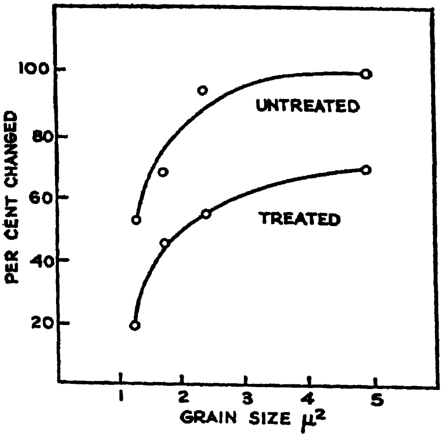

Fig. 51. The relation between the developability and size of desensitized grains.

Sheppard,[41] Wightman, and Trivelli[42] found that, by the alternate application of chromic acid and potassium iodide, sensitivity could be reduced to a minimum and the latent image almost but never quite destroyed. They became convinced that part of the latent image and part of the sensitivity substance were situated within the bulk of the grain, to be liberated only under special circumstances (p. 166).

The Nature of Sensitivity Specks

By the beginning of 1924, it was realized that the developer acts on the grains at local points, coinciding, perhaps, with the action of light, that the local points or specks represent discontinuities in the grain structure, and that most of the useful specks are situated on the surface of the grain. The question arose whether the specks are places of disruption or physical strain, points of partial reduction by degradation of the gelatin, or are composed of foreign substances.

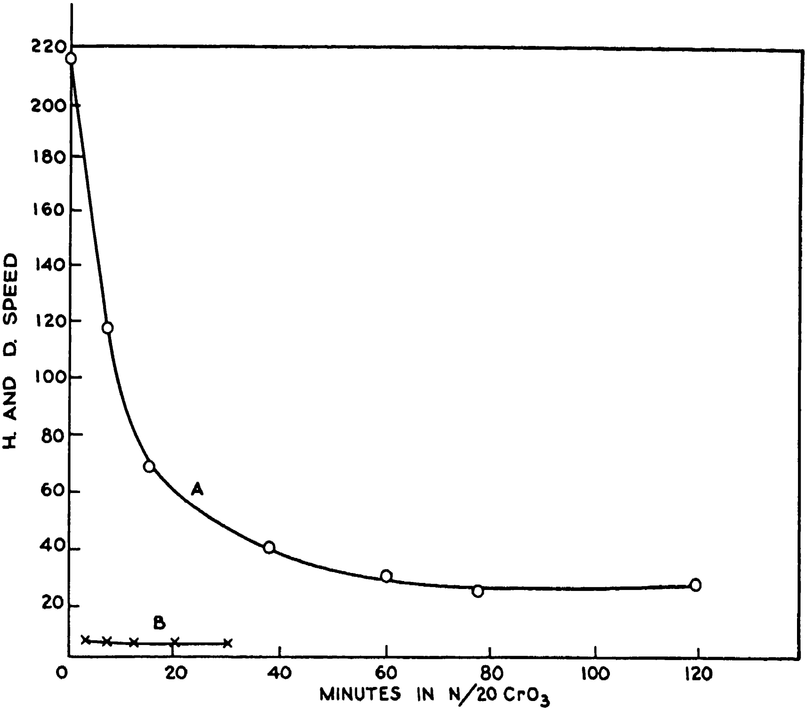

FIG. 52. The effect of chromic acid on the sensitivity of plates (A) without and (B) with preliminary exposure.

An effective solution was provided by the discovery by Sheppard (p. 95) of the presence of isothiocyanates in photographic gelatin and of their reaction with silver bromide to form double compounds of relatively low solubility. He showed that at low concentrations microscopic specks are formed on silver halide crystals, which are converted under alkaline conditions to silver sulfide. It was at least reasonable to assume that, at the still lower concentrations used for sensitizing, similar but ultramicroscopic specks would be formed.

Experiments in which emulsions sensitized with thiocarbamides were kept at low pH throughout showed very slight sensitizing, whereas an increase in the pH produced a steady rise of sensitivity. A noteworthy parallelism was found between a curve showing this and the rate at which the double compound of allylthiocarbamide and silver bromide (as a function of pH) decomposed. In general, the fact that emulsions of high speed could be prepared in the presence of thiocarbamides, under conditions of pH, temperature, and time which were found by direct experiment to convert the combinations of silver halide and sulfur body to silver sulfide, makes any other interpretation very improbable. Once the sulfide is formed, any reversible speed increase by rise of pH, such as that discovered by Rawling,[43] could not be explained as a further production of sulfide. The irreversible speed increase, however, may be attributed to the formation of silver sulfide. Even if there is no direct proof of such a reaction, the fact that conditions precluding silver sulfide formation give little or no sensitizing with thiocarbamide, while conditions which produce analyzable amounts of silver sulfide do give sensitizing, constitutes the essential evidence for the assertion.

The identification of the sensitizing substance as silver sulfide advanced knowledge by a decisive step but left the mechanism of sensitivity still to be explained. In the first experiments suggested by his discovery, Sheppard determined the quantity of thiocarbamide necessary to produce a fast emulsion and studied the way in which it combines with the silver halides. In emulsion-making, only a portion of the gelatin is used for precipitation, the rest being added when digestion and washing are completed (p. 5). The sensitivity of the emulsion is so largely dependent upon the quality of the final gelatin that it must be the sensitizer in this portion that yields the silver sulfide. Additions of artificial sensitizers are most successful if made with the later gelatin.

It is difficult to obtain satisfactory results by bathing coated emulsions instead of sensitizing the emulsion. Just sufficient sensitizer must reach each grain; otherwise, sensitivity is impaired and fog increases. If multilayer plates are bathed, it is difficult to present sufficient sensitizer to the lower grains without using far too much for the upper. Sheppard and Wightman [44] were not able to secure uniform sensitization by bathing any but specially prepared single-grain layer plates. By keeping the sensitizer acid and adding a soluble bromide to repress the solubility of the double compound, they were able, with a subsequent bath in dilute alkali, to get reasonable increases in sensitivity.

To examine the action of the sensitizer, the first requirement is an inert gelatin. Such a material does not occur naturally, although gelatin made from rabbits, which seem to dislike sulfur-bearing vegetables, is relatively inactive. Whatever the source, the gelatin must be purified. De-ashing, by treatment with alkali and acid followed by washing with distilled water, removes diffusible sensitizers. Treatment with oxidants, such as permanganate, hypochlorite, or sodium peroxide (followed by agents such as bisulfite to remove excess), destroys non-diffusing sensitizers. (Such treatments destroy also some antisensitizers, while treatment with silver bromide, useful only for research purposes, removes both sensitizers and antisensitizers.)

An emulsion is made with the purified gelatin and, at the appropriate stage, is divided into lots which are treated with varying quantities of sensitizer. The lots are coated for convenience on glass plates, dried, and examined for such photographic qualities as speed, γ, and latent fog, after different times of development. Sheppard found that very small quantities of sensitizer gave a noticeable increase in speed. One part in a million gave a detectable change, and probably not more than one part in fifty thousand is responsible for the sensitivity of high-speed emulsions. With further additions of sensitizer, the speed increased greatly; but the gain was of little use because of the increase in latent fog or spontaneous developability. The speed did not increase indefinitely; but with the incorporation of about one part of sensitizer in seven thousand of the emulsion (dry weight) a well-defined maximum was reached, after which the speed fell until, with one part in two hundred, the fog was as high as the maximum density of some of the other plates, and it was almost impossible to determine the speed. The growth of fog and sensitivity is shown in Figure 53.

Useful addition of the sensitizer does not alter the appearance of the emulsion even under the microscope. If more than 0.1 per cent of sensitizer is present, the emulsion becomes brown with silver sulfide. The distribution of the sulfide over the grains was elucidated by the studies of Sheppard, who, with Hudson[45] and Trivelli and Wightman,[46] attacked the matter from two standpoints. Hudson allowed a fused lump of silver bromide to hang in a solution of allyl thiocarbamide until, after some twelve hours, crystalline clusters of the silver bromide-thiourea complex were found growing from individual points on the surface (Figure 54). It is probable, therefore, that, when silver bromide grains are attacked by a solution containing thiocarbamide, the latter is adsorbed to the silver halide and reacts with it *in situ*[47] to form the molecular compound. It is most unlikely that, in the subsequent degradation of the compound by

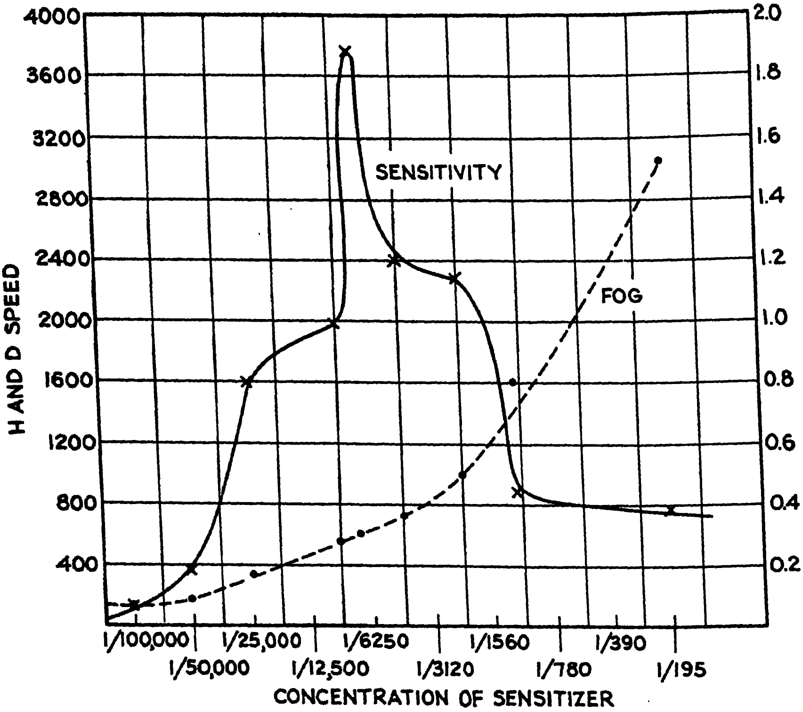

FIG. 53. The growth of fog and sensitivity in an emulsion made with gelatin containing a sulfur sensitizer.

alkali, the silver sulfide would be redistributed over the grain. The suggestion is emphatic that the sulfide is produced at points previously occupied by the double salt.

Trivelli and Wightman's experiments concerned actual emulsion grains. A single-grain layer plate was bathed for an hour in 1/100 per cent allyl thiocarbamide solution and was then treated with alkali. It was photomicrographed before treatment, after thiocarbamide, and again after treatment with alkali. The pictures (Figure 55) show that the specks are clearly visible in the second and third stages. To refute the suggestion that they are due to the intense red light from the microscope condenser, another set of grains was illuminated until they showed alteration, and the optical decomposition was compared with

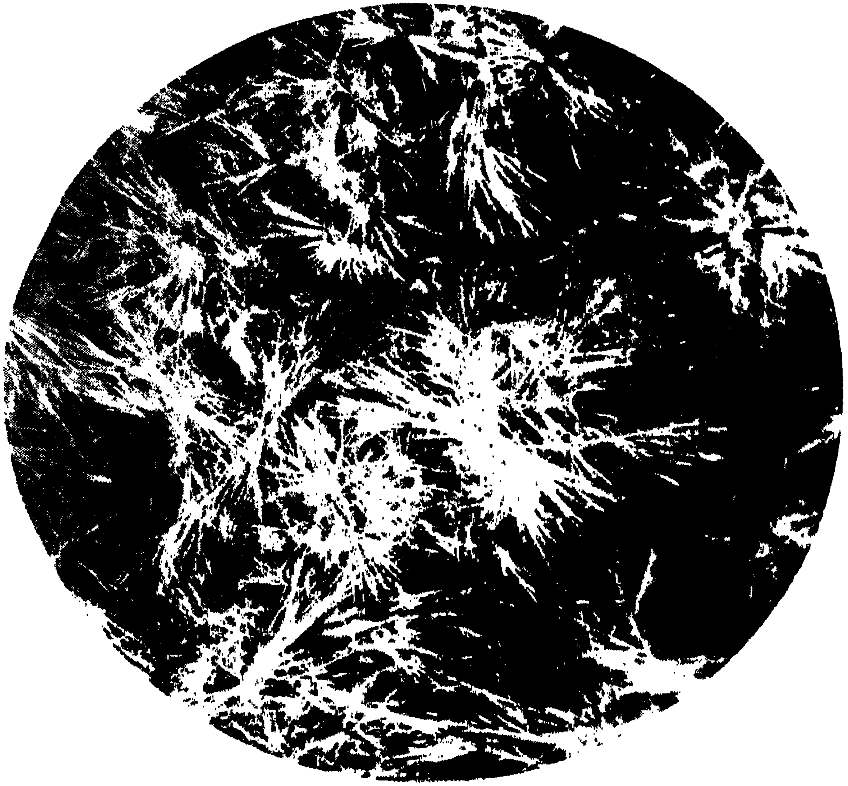

FIG. 54. Photomicrograph of crystals of the thiocarbamide addition compound with silver bromide. ×30.

that given by sulfide. There was no resemblance; the sulfide collected in a very few places, while the photochemical decomposition showed a regular pattern.

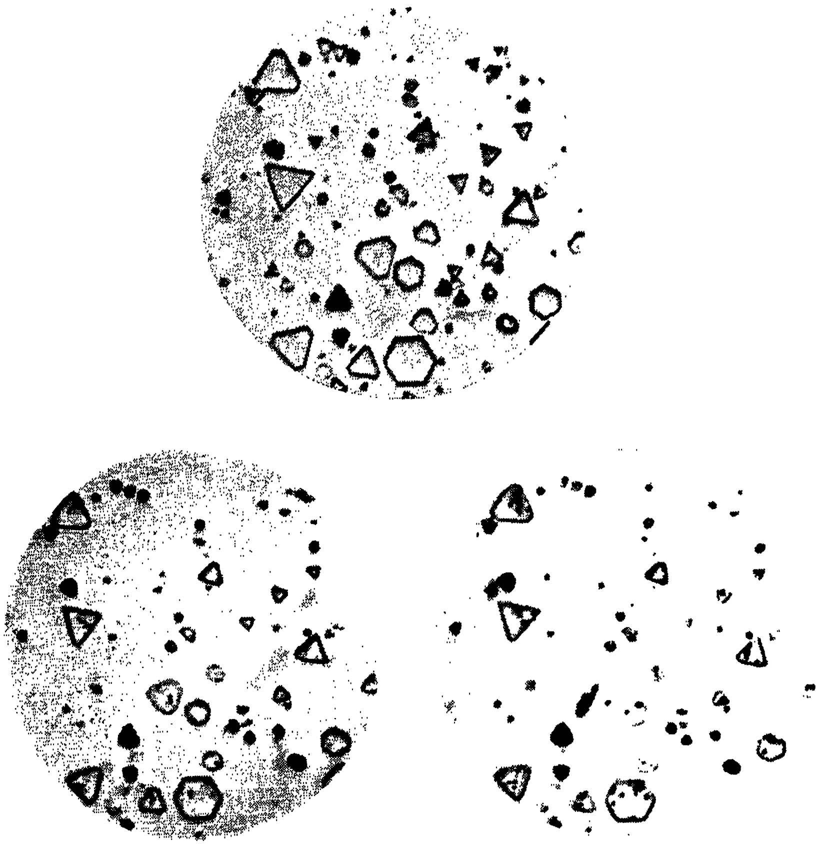

FIG. 55. Photomicrographs of silver bromide grains: *top*, original crystals; *left*, specks of the thiocarbamide addition formed on the crystals; *right*, the specks converted by alkali to silver sulfide.

In 1927, Clark [48] attempted to distinguish between the sensitivity substance and the latent-image substance. These experiments with chromic acid, which have already been discussed, had shown there was a much greater reactivity of the latent image, from which he concluded that an oxidizing solution of very low oxidation potential should not attack the sensitivity centers if they consisted of silver sulfide; therefore, such an oxidizing solution should not decrease the sensitivity of an unexposed plate but should destroy the latent image in an exposed plate if the oxidation potential were high enough for the solution to attack silver. The experimental results seemed to indicate that the unexposed grains contained not only silver sulfide but also silver, which was more easily dissolved. In this connection, Sheppard[49] and Ballard emphasized the importance of the degree of dispersion. Their experiments dealt with the attack of persulfate on colloidal silver sulfide and showed a rapidly increasing rate of attack with increasing dispersity.

The Function of the Sensitivity Specks

It being established that highly sensitive silver bromide grains have specks of silver sulfide on their surfaces, the next question is what is the function of these specks in promoting sensitivity? According to Toy's (p. 148) theory, the grains previous to exposure contain photosensitive spots which vary not only in number but also in photosensitivity. Sheppard, Trivelli, and Loveland[50] showed that the conclusions as to the relation between the number of developed grains and the exposure for grains of various sizes which follow from Toy's hypothesis are not in accord with experimental results; but an even greater difficulty arises from the fact that if the pre-existent nuclei are light-sensitive and essentially different from silver bromide, their spectral absorption should determine the spectral sensitivity of the material or powerfully affect it. The spectral sensitivity of certain plates before and after desensitizing with chromic acid according to methods already described was determined.[51] The relative spectral sensitivity in the blue-violet region was the same after desensitizing as before, this distribution corresponding to the absorption spectrum, approximately, of gelatino-silver bromide. This conclusion is confirmed by the results of Toy and Edgerton[52] that upon exposure to a mercury-arc lamp at 435.8, 406.2, and 365.0 mμ, the experimental relation between the amount of the incident light energy and the number of centers produced is that to be expected if allowance is made for the light absorption by the silver bromide grains, the agreement being improved if the light absorbed is reckoned in quanta. From this, Toy[53] drew the conclusion that the actual substance changed by light in the formation of the latent image is silver bromide—"the function of the traces of foreign matter at the centers (nuclei) is to facilitate, catalytically, the decomposition by light."

Sheppard, Trivelli, and Loveland [50] point out, however, that catalytic facilitation of "the decomposition of silver bromide by light" could not occur without either optical sensitizing (which had been disproved) or contradiction of Einstein's [54] photochemical equivalence principle, which had been shown to hold for the photolysis,[55,56] and which also agrees with Toy's spectral results. Hence, the foreign nuclei do *not* affect (1) the relative spectral sensitivity, (2) the number of quanta absorbed, (3) the number of silver atoms formed per quantum absorbed.

From these conclusions, Sheppard, Trivelli, and Loveland developed the theory that the function of the nuclei is to "*concentrate* the silver atoms reduced by the light absorbed by silver bromide." They suppose that specks of a material, probably silver sulfide but, in any case, not silver bromide, are formed on the grains during emulsification by casual adsorption and reaction with the silver bromide of a substance from the gelatin. This forms a number of specks scattered at random among the grains and further varying in size owing to the inelastic and elastic collisions of the molecules of the adsorbed substance according to the laws of probability. Once a speck is formed, it will grow, because in its immediate neighborhood the number of inelastic collisions and fruitful encounters will be relatively greater.* It can be shown that by these premises not only does the average number of specks on large grains in the same emulsion tend to be greater than on small ones, but the average size is also greater. Evidence has been obtained that the same is true for "over-size" specks, *i.e.*, for those large enough to induce "spontaneous developability" or emulsion fog.

But, with an increasing number of specks per grain, there is an increasing chance of the specks growing, and this tendency may restrict the increase in number of specks in the larger grains. In agreement with this, it is supposed that the apparent "sensitizing" action of a speck is confined to increasing its size by accretion of photochemically reduced silver atoms to form a nucleus large enough to induce developability. Hence, the less the exposure required for this, the greater the apparent "sensitivity" of the grain. The increase in average size of specks in larger grains would make it seem unnecessary to assume with Toy that if a nucleus is in a larger grain, it is more sensitive than it would have been in a smaller grain. This conception of Toy's may be reinterpreted. It depends upon the premise that the larger the silver halide grain, the larger the area illuminated, the more quanta of light absorbed, and the greater the number of silver atoms reduced and available for concentration.[57]

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* This may be easily observed in the deposition of noble metals by cathodic sputtering.

The concentration speck theory has been recognized from the beginning as an important step in the explanation of the latent-image process. Though later work has modified somewhat the view as to the details of the process whereby the latent-image silver is coagulated around the sensitivity specks, the basic idea of the concentration speck theory has not been overthrown.

The size of the sensitizing specks and the amount of silver necessary to make a grain developable were the objects of several investigations. Sheppard discussed[58] the quantity of silver which the latent image is likely to contain and compared this with the quantity of silver sulfide found by microanalysis in the sensitivity specks. The data on silver include the values of Sheppard and Wightman, values determined later by Jones and Schoen,[59] the important results of Hilsch and Pohl,[60] and a figure secured by Arens and Eggert.[61] The figures for silver sulfide content are based on experiments with two representative emulsions of the high-speed type. The grains from these emulsions, after the digestion process with gelatin containing the

TABLE VIII

THE SILVER CONTENT

Authority	*Degree of Exposure*	*Grams of Silver per Gram of AgBr*	*Silver Atoms per Grain of 1 μ² × 0.1 μ*
Hilsch and Pohl	Heavy exposure	0.5×10^{-7}	4300
	Medium "	0.5×10^{-8}	430
Arens and Eggert	$D = 1$	10^{-8}	860
Jones and Schoen	$D = 1$	0.5×10^{-8}	400
	Threshold "	0.5×10^{-9}	40
Sheppard and Wightman	" "	3.6×10^{-9}	24
	" "	2×10^{-10}	3

usual quantity of labile sulfur, were separated into three fractions by centrifuging. The grains were analyzed for silver sulfide by the methylene blue [62] method:

TABLE IX

Experiment	*Average Grain Diameter*	*Percentage Relative Mass of Fraction*	*Grams of Silver Sulfide per Gram of Silver Bromide*
1.	2.0 μ	72.2	5.95×10^{-4}
	1.0 μ	23.4	3.18×10^{-4}
	0.2 μ	4.6	56.2×10^{-4}
2.	2.0 μ	50.0	7.4×10^{-4}
	1.0 μ	46.1	5.5×10^{-4}
	0.2 μ	3.6	36.0×10^{-4}
	Ultra-fine	0.24	105.0×10^{-4}

The data set the following limits as probable: atoms of light-liberated silver in exposed grain, 1–500; molecules of silver sulfide in sensitized grain, 1,000–20,000. That emulsion grains contain much more silver as silver sulfide than is contributed as metallic silver by latent-image formation seems certain; but the distribution of the silver or silver sulfide is not taken into consideration, and they may be either distributed uniformly or concentrated in a few scattered nuclei. Accordingly, these results do not give information on the size of speck required to act as a nucleus in initiating development of the grain.

Svedberg [63] drew an analogy between the photographic nucleus for development and the reduction of gold solutions, in which, according to experiments of Zsigmondy and Thiessen,[64] the nucleus action begins when the gold particles exceed a size of about 300 atoms. According to Svedberg's ideas, the size of the silver nucleus in the latent image would have to be of the same order of size.

Reinders and Hamburger [65] attempted to determine the minimum size of silver nucleus that would initiate development by depositing silver layers of subatomic thickness by sublimation in high vacuum. The atoms in such layers are scattered haphazardly, mainly as single atoms but also in groups of two, three, four, or more atoms with decreasing frequency. Reinders and Hamburger calculated the distribution of atoms in such subatomic layers by the probability theory. They assumed that the atoms of the extremely dilute silver vapor upon striking a glass surface at low temperature remain where they strike. On a surface which has room for n atoms in a closed monatomic arrangement, Bn atoms are deposited (B = thickness of layer decided upon); and aggregates of A atoms can be formed by atoms touching or landing upon one another. If x is the part of the surface covered by these aggregates, from probability considerations it can be shown [66] that for small values of B ($B < 0.01$),

$$x = p \frac{B^A}{A!} e^{-B},$$

in which the factor p has the value 1 for single atoms, $p = 7$ for double atoms, $p = 7 \times 10$ for triple atoms, $p = 7 \times 10 \times 12$ for quadruple atoms, etc. For $B = 0.005$ and for a surface area of 10 μ^2, there would be about 771,000 single atoms, 14,000 double atoms, 235 aggregates of 3 atoms, and 3–4 aggregates of 4 atoms. For $B = 0.001$, there would be 160,000 single atoms, 500 double atoms, and 2 aggregates of 3 atoms.

Reinders and Hamburger produced layers varying from $B = 0.001$ to $B = 0.2$ on glass plates and subjected these layers to physical development (freshly prepared solution of 1.5 gms. hydroquinone and 0.2 gm. gum arabic in 100 cc. distilled water to which 1 cc. of a 25 per cent silver nitrate solution had been added several seconds before use. The temperature of development was 20° C.; development time, 8 minutes with automatic agitation). They found that physical development of these thin layers becomes possible when the layers reach an average thickness of 0.001 to 0.005 atom. From this fact and microscopic observation of the developed layers, they concluded that isolated silver atoms do not act as nuclei and the developability of an aggregate of silver atoms begins when the aggregate contains three or more atoms. In the developed layers of 0.005 atom thickness, it was observed that the ultramicroscopic grains were distributed so that approximately three or four were present per 10 μ^2 area. The probability calculation for this case gave about three to four aggregates of four atoms in the same area.

In later work by Reinders and DeVries,[67] the above experiments were repeated with greater refinement, the lower limit of the silver nucleus being set at four silver atoms.

In an evaluation of the work of Reinders and Hamburger and Reinders and DeVries, it is to be borne in mind that their conclusions rest on the assumption that atoms which strike a surface become fixed as soon as they touch the latter. This assumption is open to question. Condensing atoms and molecules may remain for a short time in violent motion along the surface of the support. The presence of this "adlineation" would, of course, invalidate the calculations quoted above. Moreover, the experiments just reported apply to the case of physical development of a silver nucleus situated on a glass plate, separate from silver bromide. It seems probable that the size of nucleus required to start development when the silver is adsorbed to silver bromide and, furthermore, is protected to some extent by the charged grain surface and the adsorbed gelatin might be different from the value of three to four atoms found in these experiments. Indeed, a gradual transition in initial reactivity to development might be expected from the unexposed grains to the well-exposed ones. The interface condition is not the same when the silver nucleus consists of two or three atoms as when it consists of several thousand. Up to a certain limit, which should be reached by the time the silver nucleus is composed of a few hundred atoms of silver, the interface reactivity increases as the size of the nucleus increases. There is, therefore, no justification for speaking of a "critical" size which the latent-image nucleus must attain before a grain becomes developable; all of the grains are developable, but to a different degree. This is true, of course, of only the very early stages of reduction of the individual grains. Once the silver nucleus has attained sufficient size, the rate of reduction of the grain should be independent of the amount of exposure which produced the original nucleus.

QUANTUM EQUIVALENCE IN THE PHOTOLYSIS OF SILVER BROMIDE

In any theoretical study of the photographic process, consideration must be given to the experimental evidence for the validity of the quantum equivalence law in the photolysis of silver bromide and its applicability to sensitivity and also to the relation between the absorption of light and the photocurrent produced.

In 1921, Eggert and Noddack [55a] showed that the number of silver atoms produced in the photolysis of silver bromide or chloride is equal to the number of light quanta absorbed by the silver halide. This agrees with the photochemical equivalence law of Einstein (p. 178).[54] This applies only to the direct action of light, and the photolysis of silver halide is one of the few cases where the validity of the law is not obscured by subsequent reactions. The experimental difficulties in the determination of the quantum equivalent are very considerable. They arise in connection with the absorption of light in a turbid emulsion, with the analytical determination of the minute mass of silver produced, and with the necessity for removing the halogen by an acceptor to prevent recombination.

The validity of the photochemical equivalence law was confirmed in later investigations by the same authors [55] and by Mutter.[56] Mutter used silver bromide precipitated in the absence of any binding material and, therefore, added sodium nitrite to react with the bromine liberated. In the presence of gelatin, such an absorbing agent is not so necessary. Table X shows the results obtained by Mutter:

TABLE X

QUANTUM YIELD (ϕ) FROM FREE PRECIPITATED SILVER BROMIDE FOR AN (INITIAL) ABSORPTION OF 50 PER CENT RADIATION OF 436 mμ

$h\nu$ *Incident*	*in* H_2O (5% $AgNO_3$ *in* 5% KBr)	*in* $NaNO_2$ *Solution* (5% $AgNO_3$ *in* 5% KBr)	*in* $NaNO_2$ *Solution* (35% $AgNO_3$ *in* 5% KBr)	*in* $NaNO_2$ *Solution* (40% KBr *in* 5% $AgNO_3$)	Ag^+-*body*
0.5×10^{17}	0.16	0.60	0.92	1.20	1.20
1.0×10^{17}	.16	.56	.92	1.20	0.92
2.0×10^{17}	.15	.55	.90	1.10	.76
3.0×10^{17}	.14	.53	.80	—	.50

The lowest values of the quantum yield are in column 2, where water is the only halogen acceptor, which, as noted later, is quite inefficient. The series in column 6 is interesting because of the more rapid fall with increasing exposure. Here the only halogen acceptor besides water is the adsorbed silver ions, the capacity of which would be quite limited.

These and the other researches referred to indicate a maximum quantum equivalent of unity ($\phi = 1$). In the aqueous systems considered, the chief halogen acceptance reactions may be regarded as

$$\left.\begin{array}{l} Br + Br \rightarrow Br_2 \\ Br_2 + H_2O \rightleftharpoons Br^- + OBr^- + 2H^+ \end{array}\right\} \quad I$$

Since OBr^- (hypobromite) is an active brominating and oxidizing substance, it is evident that in water alone the quantum yield could not approach the maximum. The effect of bromide and hydrogen ions on the equilibrium is significant, as noted later.

If nitrite ions are added, it may be assumed that the following reactions will occur:[56]

$$\left.\begin{array}{l} Br_2 + 2\,NO_2^- \rightarrow 2\,Br^- + N_2O_4 \\ N_2O_4 + H_2O \rightarrow H^+NO_2^- + H^+NO_3^- \end{array}\right\} \quad II$$

or

$$OBr^- + NO_2^- \rightarrow Br^- + NO_3^-$$

(via reaction system I)

THE DISTRIBUTION OF THE LATENT IMAGE IN THE SILVER BROMIDE GRAIN

The validity of the quantum equivalence law for the silver produced by the photolysis of gelatin silver bromide suggests that this law must be valid also in the case of the much shorter exposures required for the production of a latent image. The effectiveness with which the latent image, however, causes developability depends not so much upon the mass of silver produced as upon its distribution among the collecting centers at the surface. There is strong evidence that latent-image specks may be formed within the grain as well as on the surface; but in the absence of any solvent in the developer, only the surface image can initiate development.

In 1894, Kogelmann[68] dissolved away the surface of the grains to reveal to the developer latent-image nuclei below the surface of the grain. In 1891, Lainer[69] noticed that small quantities of iodide added to the developer increased the amount of density or, perhaps, latent image which could be developed. von Hübl,[70] Lüppo-Cramer,[71] and Sheppard[72] examined the action of very dilute iodide previous to development. Lüppo-Cramer suggested that any intensification was due to the opening up of the grain by the formation of silver iodide, since it has a different specific volume. Straining the surface or accumulating in the fissures, it might reveal internal nuclei which would not act in the ordinary way as development centers. Renwick,[73] however, was able to convert an ordinary bromo-iodide plate, which consists chiefly of silver bromide, into silver iodide by immersion in potassium iodide solution without completely destroying a latent image. He used sulfite in the solution to reduce any iodine liberated from the iodide. The experiment was valuable as showing that the latent-image substance itself was not a silver halide and that it was stable in the presence of a mild reducing agent. Earlier, Lüppo-Cramer [74] had demonstrated that a latent image apparently destroyed by chromic acid could be revived by treatment with dilute iodide before development. Two sets of plates were exposed behind a step wedge (the Chapman-Jones plate tester [75]), treated with chromic acid solution, and one set further treated with 1 per cent of potassium iodide. After prolonged development, no trace of an image appeared unless the iodide was used, in which case as many steps became visible as by development of a completely untreated control plate. This supported the contention that the iodide had laid bare nuclei in the interior of the grains, where they had remained protected while in the desensitizing bath. Kempf [76] made a study of the topographical distribution of the latent image by treating the grains of an exposed photographic emulsion alternately with silver and silver bromide dissolving solutions. In this way, the latent-image substance on the grain surface was alternately destroyed and made to appear again. Kempf demonstrated that the latent image is distributed throughout the grains, its concentration decreasing toward the center of the grain. With X-ray exposures, he found the decrease of latent image with depth to be more rapid than with visible light. Kempf used emulsions with especially large grains, not normally used in photography, which he prepared with inert gelatin.

The distribution of the latent image between the surface and interior of the grains of some commercial emulsions was investigated by Kornfeld.[77] The densities of two exposed strips of the same film were compared after post-fixation physical development, one strip having been treated with ammonium persulfate after exposure. For low exposures, the density produced by the centers in the interior of the grains was only a very small part of that produced by the untreated grains. Thus, practically all the sensitivity specks are present at the surface of the grains, which agrees with the fact that the growth of the grains is completed before the "after-ripening" sensitizing gelatin is applied. Previous estimates suggested that the sensitivity at the surface of the silver bromide grains is less than one one-hundredth part of the sensitivity of the whole grains, but there appears to be no evidence for this suggestion. At higher exposures, the density from the centers in the interior of the grains increases considerably.

Lüppo-Cramer [78] suggested that the reciprocity law failure at high intensity is to be attributed to the formation of increasing amounts of latent-image nuclei in the interior of the grain with increasing intensity, so that with ordinary developers, which act mainly on the grain surface, a loss of speed results. Lüppo-Cramer further proposed that the Clayden effect is caused by the formation of internal latent-image nuclei. He assumed that the first high-intensity exposure to light forms nuclei in the interior of the grain and that upon the second exposure to weak light these interior nuclei act as sensitivity centers for the latent image, thus producing the desensitization observed in the Clayden effect. Lüppo-Cramer gave no experimental results to support his views. Landau,[79] however, had arrived at the same conclusions regarding the Clayden effect from experiments in which he had used chemical and post-fixation physical developments. Stevens [80] also showed that the Albert effect, which is produced when an exposed film is subjected to a bleaching agent and then given a second uniform exposure before development, is caused by the existence of internal latent-image nuclei (p. 296).

These experiments demonstrated that latent-image nuclei are formed in the interior of the grain as well as on the surface and showed, further, that these internal nuclei are of importance in certain photographic effects. In fact, interpretations of results relating to latent-image formation generally might be seriously affected if the influence of these internal latent-image nuclei is ignored.

In 1941, Berg, Marriage, and Stevens [81] developed a technique for separating the surface and internal latent images and applied it to various photographic effects. They considered distinction between the surface and internal latent images sufficient without a determination of the actual distribution of nuclei below the surface and used the following three types of solutions:

1. A "surface developer" which, as far as possible, contained no silver halide solvent and should thus affect only grains carrying a surface latent image.
2. A bleach which would dissolve only the latent image shown by the surface developer and leave the internal image, as far as possible, unaffected. This solution contained no silver halide solvent.
3. An "internal developer" containing silver halide solvent so adjusted in concentration that the surface of the grains was gradually etched away, allowing the internal image to appear on the new surface of the grains and causing them to be developed.

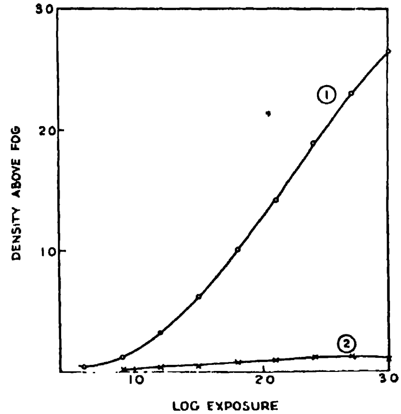

FIG. 56. Characteristic curves for the development of the surface latent image treated with a bleaching solution: (1) dilute bleaching solution; (2) concentrated solution.

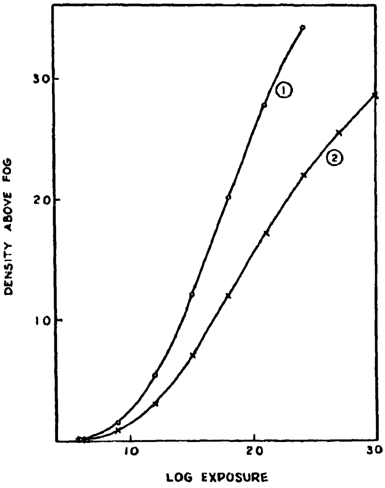

FIG. 57. Characteristic curves for the internal latent image treated with a bleaching solution: (1) dilute solution; (2) concentrated solution.

As surface developers, sulfite-free catechol and carbonate, and hydroxy-phenylglycine solutions were used. Glycin was the most effective in distinguishing between the surface and internal latent image. The bleach consisted of a combination of sulfuric acid and potassium dichromate. The proportions of these two constituents had little effect on the results. For the internal latent image, a fairly energetic metol-hydroquinone-carbonate developer was used, to which thiosulfate was added as a silver halide solvent.

The effectiveness with which the solutions could distinguish between surface and internal latent-image nuclei may be seen from the curves of Figures 56 and 57. The characteristic curves were derived from sensitometric strips treated with (1) a dilute bleaching solution and (2) a concentrated bleaching solution. For Figure 56, the surface developer was used, and the latent image on the strip treated with the concentrated solution is seen to be almost destroyed. For Figure 57, however, the developer containing a solvent developed the internal latent image even on the strip treated with the concentrated bleach. Thus, the surface and internal latent images can be distinguished by the proper concentration of bleaching solution, which must be determined for each emulsion used.

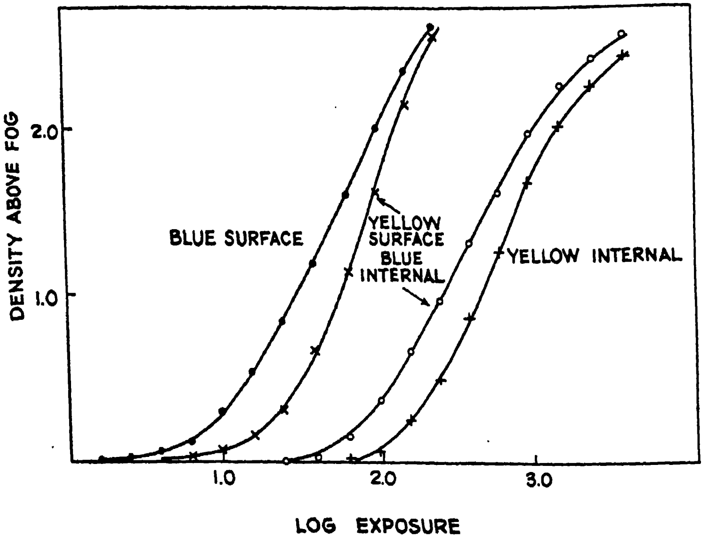

FIG. 58. Characteristic curves for the surface and internal latent images exposed to blue and to yellow light.

That the distribution of the latent image is unaffected by sensitizing dyes used to produce an image by light of wave lengths which do not normally affect silver bromide is shown by the results given in Figure 58. A material sensitized for yellow light was exposed through blue and yellow filters and developed to reveal the surface and internal images for both colors. It is seen that the distribution of the image produced by yellow light, by means of the dye, is the same as that produced by blue light. This agrees with results reported by other workers.[82]

THE INFLUENCE OF TEMPERATURE ON THE LATENT IMAGE AND ON PHOTOLYSIS

Berg, Marriage, and Stevens studied the change of distribution of centers in the grain with the change of temperature by making comparison exposures at room and liquid-air temperatures (90° K.). The loss of sensitivity with lowered temperature was much greater in the case of the surface latent image than of the internal latent image. The results are shown in Figure 59 for a low intensity level, where the difference between change of internal and surface latent image was especially pronounced. Relatively little work has been done on the effect of temperature on direct photolysis; but the results obtained indicate a con-

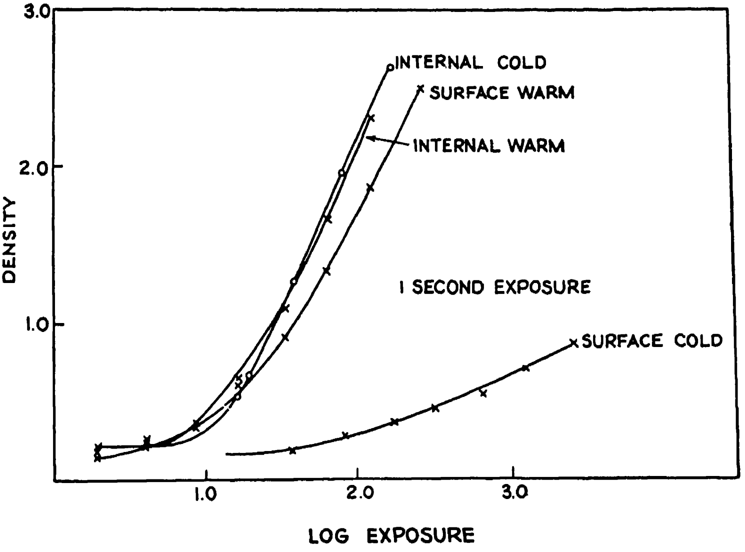

FIG. 59. Characteristic curves for internal and surface latent images exposed at high and low temperatures.

siderable decrease in the production of photolytic silver at low temperatures, although the effect of very low temperatures does not seem to arrest the reaction as completely as it does the production of the latent image. Löhle [83] and Cameron and Taylor [84] observed that practically no visible darkening of silver chloride occurred when it was exposed to ultraviolet light at temperatures of − 120° C. and below, and direct measurements of the photolytic silver in gelatino-silver bromide by Sheppard and Walker * showed a rapid decrease in the silver formed upon passing from room temperature to that of liquid air (− 183° C.).

THE INFLUENCE OF THE REMOVAL OF HALOGEN ON SENSITIVITY

Since increasing exposures tend to increase the deposition of silver in the interior of the grains compared with the surface, the total amount of photolytic silver is not greatly affected by amounts of free halogen which are sufficient to prevent development by the formation of a silver halide surface on the grain. In agreement with this fact, the quantum equivalence law was found to hold for photolytic silver under largely varying conditions, whereas photographic sensitivity was found to be very susceptible to such a change of conditions. This difference undoubtedly exists, even if the validity of the quantum equivalence law for photolytic silver does not extend over the entire range of halogen pressure which was found to be without influence in previous experiments. Experiments by Sheppard, Lambert, and Walker † on the influence of an increase of temperature above room temperature on the production of photolytic silver in gelatino-silver bromide layers show that at temperatures above 25° C. the amount of photolytic silver increases considerably. At such temperatures, gelatin may be expected to react more quickly with halogen. This necessarily means that at room temperature the quantum yield, ϕ, was less than unity. Possibly, however, the exposure was too great in these experiments.

In 1926, Rawling and Glassett [43] discovered that adjustment of the hydrogen-ion activity (pH) of an emulsion immediately prior to coating and drying produced a reversible effect on sensi-

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* Unpublished observations.

† S. E. Sheppard, R. H. Lambert, and R. F. Walker, private communication.

tivity, in the sense of increased sensitivity by elevation of pH, decreased sensitivity by reduction of pH. This effect can be distinguished definitely from an irreversible pH effect on sensitizing in digestion. Soon afterward, Sheppard and Wightman [85] established a reversible bromide ion (pAg $\sim$ pBr) effect on sensitivity, wherein increased Br^- ion activity (increased pAg or decreased pBr) diminished sensitivity, while lowered Br^- ion increased it. These two reversible effects were discussed together in 1931 by Price,[86] who presented a theory relating them to processes of halogen acceptance.

Another reversible effect on sensitivity, of which some account was noted early, is that of atmospheric humidity.[85] Observations regarding this, however, have been discrepant and even contradictory. The reason for this was given by Sheppard and Graham.[87] They show that the reversible moisture effect is essentially connected with the reversible pH and pAg effects, and that consistent observations can only be made when these two factors are controlled. This is brought out by two curves showing the effect of relative humidity on the photographic sensitivity (inertia speed) of an emulsion (*a*) of constant pAg adjusted to various pH values (Figure 60) and (*b*) of constant pH adjusted to various pAg values (Figure 61). It is evident that (1) susceptibility to moisture influence depends upon the pH and the pAg of an emulsion; (2) that the sensitivity (speed) passes through a definite maximum in the neighborhood of 20 per cent R.H. at room temperature.

It was suggested by Price [86] that the reversible pH and pAg effects could be explained in terms of the kinetics of bromination of gelatin. For the primary reaction of bromine with water, the equilibrium may be assumed to be

$$Br_2 + H_2O \rightleftharpoons HOBr + HBr$$

or

$$Br_2 + H^+ + OH^- \rightleftharpoons 2H^+ + Br^- + OBr^-;$$

whence

$$[OBr^-] = \frac{k[Br_2][OH^-]}{[H^+][Br^-]}$$

$$= k' \frac{[Br_2]}{[H^+]^2[Br^-]}.$$

The most probable reaction with gelatin is of the form

$$\text{Gelatin} + \text{OBr}^- \rightleftharpoons \text{Gel Br} + \text{OH}^-,$$

though the above equation is an extremely simplified representation of the facts. Price pointed out that qualitatively these

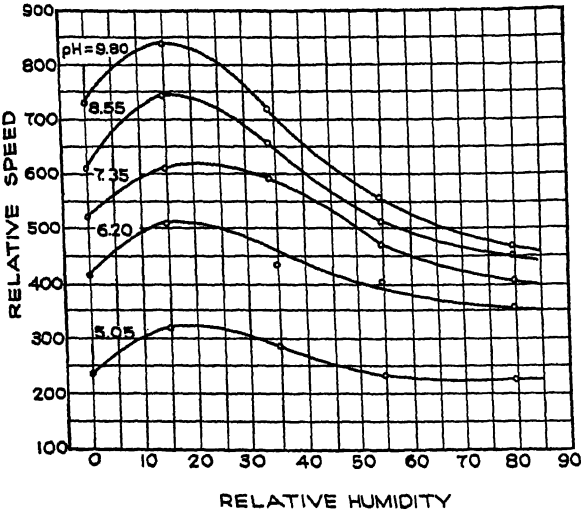

FIG. 60. The relation of sensitivity to relative humidity at various pH values.

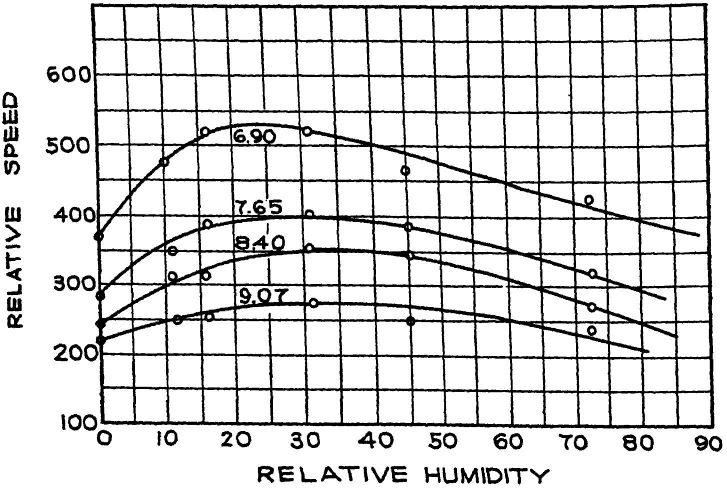

FIG. 61. The relation of sensitivity to relative humidity at various pAg values.

reactions would explain the reversible pH and pAg effects. Sheppard and Graham [87] suggest that the effect of moisture is also in agreement, in that water is essential to the primary hydrolysis of bromine, but more than a certain amount simply dilutes the active hypobromite and lowers its rate of reaction. In the same paper is discussed the possibility that silver sulfide rather than gelatin might be the effective halogen acceptor.[88] This is discounted, however, by the observation that the attack of aqueous bromine on silver sulfide is diminished instead of increased by raising the pH.

The evidence that the formation of the developable latent image is very considerably affected by the kinetics of halogen acceptance has certain important general consequences. It is evident that restriction of the theory of latent-image formation to intragranular processes of nucleus formation and growth is unjustified. The processes of halogen removal are undoubtedly strongly susceptible to temperature, and an unknown proportion of the effects of temperature on latent-image formation must be accredited to them.

THE INTERNAL PHOTOELECTRIC EFFECT

In the early days of photoelectricity, it was suggested that the silver bromide grain might lose electrons in the same way as a potassium or platinum surface exposed to light [34] and that the latent image consisted of grains which had lost negative electricity. No mechanism was proposed to explain the fact that this process is not completely reversed after the light is removed. Toy [89] and his collaborators showed that the external effect in the ultraviolet region is not connected with photographic sensitivity. Against the conception of an external photoelectric effect, Fajans and von Beckerath [90] and Sheppard and Trivelli [91] independently suggested an internal photoelectric effect as the mechanism of photochemical change in silver halide crystals – a shifting of electrons when radiation quanta are absorbed, which results in the transfer of electrons from bromide to silver ions.

The main conception of the external photoelectric effect, the removal of a negative charge, is emphasized again by Schwarz [92] as the condition required for developability. The charge of the grain as a whole is supposed to remain unchanged, but the charge is removed from the surface to the interior of the grain. Contributions of James[93] to the theory of developability suggest, however, that the influence of surface charge on developability is of a secondary nature.

The experimental evidence for the internal photoelectric effect is given by photoconductance phenomena and photovoltaic effects. They prove that the absorption of light produces free electrons or, at least, liberates electrons to such an extent that they can pass from one ion to another in a given potential gradient.

It has been known for a long time that silver bromide shows increased conductivity upon exposure to light. Toy[94] demonstrated that the spectral sensitivity of this effect and that of the photographic process agree in the region of their long-wave threshold and concluded that the photoconductance effect in silver bromide constitutes the primary process of latent-image formation.

Photovoltaic studies by Sheppard and Vanselow[95] confirmed this view. They measured the electromotive force produced between two similar silver-silver bromide electrodes electrolytically connected when one of the electrodes is exposed to light. A detailed study showed that

1. Upon exposure, the lighted electrode becomes instantaneously negative to the dark electrode, but this polarity reverses very rapidly, the lighted electrode becoming positive;
2. The reversal of polarity is reduced or eliminated by the introduction of halogen acceptors in the electrolyte;
3. The positive effect can be imitated in the dark by introducing halogen (bromine) into the electrolyte.

It was concluded that the *negative* effect is produced by photoelectrons transferring to the adjacent silver metal, while the *positive* effect, which follows in the absence of halogen acceptors, is due to the attack of bromine on the underlying silver metal, the positive effect corresponding to the free energy of the reaction

$$1/2\,Br_2 + Ag \rightarrow [Ag^+Br^-].$$

Figure 62 exhibits time curves of the photovoltaic effect in the absence and presence of a halogen acceptor.

The discovery of the production of photocurrents suggested a mechanism for the liberation of silver at certain discrete points by light absorbed at random all over the grain. To explain this, Sheppard [95c] had introduced previously the idea of the transfer of energy by radiationless collisions. That is, a light quantum incident at a point remote from a speck is supposed to be absorbed by the electron of a bromine ion and to raise its energy state to a higher level. This energy is then assumed to be transferred by radiationless collisions from one atom to another until the edge of a speck is reached. At this point, it is supposed that the electron of the bromine ion is completely released and the photochemical reaction occurs:

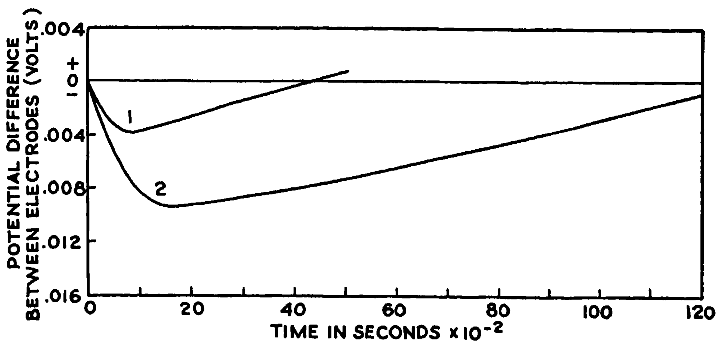

FIG. 62. The photovoltaic effect in the (1) absence and (2) presence of a halogen acceptor.

$$Br^- + h\nu \rightarrow Br + \text{electron},$$
$$Ag^+ + \text{electron} \rightarrow Ag,$$

the electron transfer from the bromine ion to the silver ion giving a neutral atom of silver.

Because of the photocurrents, Sheppard and Trivelli [91,41] advanced the idea that the electrolytic migration of ions through the crystal might take part in the formation of the latent image; and Trivelli,[96] making use of the properties of photoconductance and electrolytic conductivity of silver bromide, outlined a novel mechanism for the transfer of silver and its concentration based on an electrolytic-cell type of action. Fundamental to his theory is the idea that the sensitivity specks consist initially of silver sulfide and a trace of silver. The silver sulfide is assumed to act as anode, and the silver speck as cathode, of a cell of which the solid silver bromide constitutes the electrolyte. Upon exposure to light, electrons pass from the silver sulfide through the silver bromide to the silver, while silver cations of the silver bromide pass from the silver bromide to the silver cathode. Thus, the silver speck originally present is assumed to grow by electrolytic deposition of silver until it reaches a developable size. Certain features of this cell action are not entirely satisfactory from a theoretical point of view, and it has never been proved that it takes place in a large-scale cell of the same constitution. Though this theory has certain very attractive features, it has never been generally accepted.

PHOTOCHEMICAL CONSIDERATIONS RELATING TO THE PRODUCTION OF THE LATENT IMAGE

It has been shown in the preceding pages that when light is absorbed in silver bromide, electrons are liberated and then transferred to silver ions, which are thus converted into silver atoms, and that the number of silver atoms formed is equal to the number of light-quanta absorbed.

In 1912 Einstein [54] stated that the number of molecules reacting under the influence of light in a photosensitive system should be equal to the number of quanta absorbed. This is known as the law of quantum equivalence. It has been tested in many photochemical investigations but found to be valid only in a few cases. It did not attain its real importance in photochemistry until it was recognized as undoubtedly valid for the primary process, thus providing a possibility for the study of secondary reactions with a quantitative knowledge of their starting points. Its validity for the primary process connected with absorption can, in reality, be derived from a combination of Grotthus' and Draper's law with Planck's law of quantum absorption. Grotthus in 1817 and Draper in 1841 stated that rays of light could produce a chemical change in a system only when they were absorbed. This follows from the law of the conservation of energy, which, however, was not recognized until 1842. The introduction of the theory of absorption and emission by quanta dates from 1900. Planck postulated that radiant energy is absorbed or emitted only in discrete units, the size of which depends upon the frequency of the radiation. Each such unit, or *quantum*, has the energy content $h\nu$, where h is a universal constant and ν the frequency of the radiation. A model for the quantized absorption and emission of radiant energy, the foundation of modern quantum mechanics, was supplied in 1913 by the Rutherford-Bohr model of the atom. This and the models for molecules, introduced some time later, made it possible to visualize the connection between the primary acts of emission or absorption and the structure of the corresponding spectra.

There are three different primary processes which may accompany the absorption of light in a molecule:

(1) an electron can be raised to a higher level, creating an excited state of the molecule;

(2) it can be dissociated entirely from the molecule, creating an ion; or

(3) the raising of the electron can affect the vibrations of the atoms in the molecule to produce dissociation of the molecule.

These three primary acts—excitation, ionization, and dissociation—follow the law of quantum equivalence. The secondary reactions, however, decide whether the products of these primary processes can be preserved. An excited molecule rarely lives longer than 10^{-8} seconds before it loses its energy in reemission or fluorescence. If it collides with another molecule before that, the energy will either be dissipated by transformation into heat or used as chemical energy for the first molecule alone, for both together, or for the second molecule alone. This last case, called *optical sensitizing*, includes the possibility of the second molecule emitting the energy as fluorescence.

The products of ionization and dissociation are frequently very active. They may either recombine or undergo further reaction. This further reaction may stabilize the results of the primary process. This is what occurs in the formation of the latent image, where the one primary product, the electron, joining a silver ion, forms a silver atom which is stable if the bromine atom has no opportunity for recombination. Thus, one silver atom is found per quantum absorbed.

In many photochemical reactions, however, the active products react to form further active products, which, in their turn, undergo a similar reaction. Such a chain reaction can multiply the primary effect many times, and it might appear favorable to use such a reaction for photographic purposes instead of leaving the multiplication factor to development. But chain reactions are generally very sensitive toward traces of impurities, and it is difficult to control them accurately. There is also danger of diffusion, which would interfere with definition.[97]

The Primary Process and Spectral Absorption

In the last twenty years, much light has been thrown on the connection between the absorption spectrum and the primary process. In the case of mono- and diatomic gases, the spectrum presents a fairly clear record of the process accompanying absorption. The simplest case is that of a monatomic gas, where there are only two possible processes: excitation and ionization. A series of discrete lines represents the transition of the electron to the discrete energy levels, and the frequency values of the lines measure the necessary energy. With increasing distance from the nucleus of the atom, the energy difference between the electron levels decreases and, accordingly, the absorption lines grow denser toward the short-wave end of the spectrum. Finally, when the electron reaches such a distance from the nucleus that it is outside the sphere of attraction, no energy is required to remove it further. This occurs in the case of ionization, presented in the spectrum by the limit of the series toward which the lines are converging. Beyond this limit, the absorption is continuous, since the electron can be dissociated from the atom with any amount of translational energy. The spectrum of a diatomic gas is more complicated, but it contains much valuable information on the primary process and even on the structure of the diatomic molecules. The change of electron energy is accompanied by a variety of changes in the energy of vibration and that of rotation in the diatomic molecule, so that the raising of an electron to a higher level, which is represented by a single line in the absorption spectrum of the monatomic gas, is represented by a whole system of bands in the absorption spectrum of a diatomic gas. Information as to the binding force of the two atoms and their distance from each other in the normal and excited states can be obtained from the structure of these bands.

Dissociation of the molecule into its atoms, with continuously varying amounts of kinetic or translational energy, is represented by continuous absorption. The long-wave limit of this continuous absorption gives the energy necessary for the dissociation. If the electronic energy levels of the dissociation products are known, the energy of dissociation of the molecule in its normal state can be calculated with great accuracy; and this has been done in many cases. If, on the other hand, the energy of dissociation is known from other sources, the long-wave limit of the continuous absorption gives a method of calculating the electronic levels of the dissociation products. Since these levels are related to their electronic levels in the normal state of the molecule, knowledge of the energy state of the components of diatomic molecules can be obtained from the absorption spectrum. From an investigation of the absorption spectrum of silver chloride, silver bromide, and silver iodide in the gaseous state at sufficiently high temperatures, Frank and Kuhn [98] came to the conclusion that these halides are so-called "atom molecules," instead of "ion molecules," as would be expected. This does not mean that the distribution of charge in the molecule is completely symmetrical, as in homopolar molecules which consist of identical atoms. A shift of charge certainly takes place in a silver halide molecule, but the electron does not detach itself from the silver atom to form a halide ion; the linkage is essentially between a silver and a halogen atom. On the other hand, the absorption spectra of gaseous alkali halides show them to be true ionic molecules, consisting of alkali ions and halide ions.

Few of these outstanding differences are preserved in the crystallized state. Only silver iodide shows largely homopolar binding in the lattice, at least in the β-modification, which is stable below 145° C., but both silver chloride and silver bromide form definite ionic lattices as crystals. These ionic lattices are not quite so pronounced as in the crystals of the alkali halides, however; to a very small extent, the electron of the halide ion must be shared by the silver ion. One of the outstanding experimental differences between alkali halides and silver halides is the photoconductance shown by the silver halides. Sheppard and Vanselow [99] suggested that the light absorption of the silver halides is affected by the presence of a "virtual" metal field (of the silver cation) which arises from, and is active during, the exposure to light.

The change in the binding force which occurs when gaseous silver chloride and silver bromide are transformed into solid crystals shows the presence of considerable forces in the crystal lattice. These can be expected to produce a fundamental change in the conditions for absorption. In the gaseous state, the absorption spectrum represents only the single molecules, since they spend most of their time outside the spheres of influence of the other molecules. With increasing pressure, a broadening of the lines can be observed, which sometimes obscures the finer structure. In a crystal lattice, these influences are decisive.

Herzfeld and Wolf[100] give a method for calculating the long-wave absorption limit of the silver halides from the energy necessary for the internal photoelectric effect. Ions in a crystal lattice are supposedly held together partly by electrostatic forces and partly by so-called "Van der Waals' forces of molecular attraction." The authors assume that for the release of an electron from a bromide ion, not only the electron affinity of the halogen atom must be overcome but also the electrostatic part of the lattice energy, ϕe. This latter value could be calculated from electrostatic potential theory[101] or thermochemically, thermochemical data also being available for the calculation of the electron affinity of the halogen, E_x. Accurate absorption measurements were not available, but the equation $h\nu = \phi e + E_x$ did not seem to be supported by the available data, and the authors concluded that more factors were effective, especially the ionization potential of the cation, I_{Me}.

Accurate measurements of the absorption spectra of alkali halides and silver halides were published by Hilsch and Pohl.[102] The bands of the silver halides are much less sharp than those of the alkali halides; they resemble those of dyes in the visible region, and the extinction coefficients at the maxima are very high, approaching those of metals. The maxima of the longest wave bands for the silver halides fit the equation

$$h = \phi e + E_x - I_{Me},$$

ϕe being calculated from electric potential theory. von Hippel[103] and various other authors, however, considered this result a coincidence arising from the mutual canceling of other terms connected with the energy status of neighboring ions and the consequent neutral atoms. Hilsch and Pohl[60] themselves drew attention to the large degree of interaction between ions, which results in a crystal of high refractive index lacking the high potential barriers between neighboring ions characteristic of ionic crystals. The following table gives some idea of the magnitude of this deformation by comparing the electrostatic part of the lattice energy as calculated from thermochemical data (second column) and from electrostatic potential theory (third column) according to the formula of Madelung for a simple cubic lattice. The differences are given in the fourth column, and in the fifth column are given the differences between silver and sodium salts[104] for the electrostatic lattice energy as another measurement of deformation energy.

TABLE XI

Salt	$\phi e(T)$	$\phi(\epsilon)$	Δ_1	Δ_2
Silver chloride	9.96	9.03	0.93	1.99
Silver bromide	9.60	8.58	.92	1.31
Silver iodide	9.46	8.35	1.11	1.51

An expression for the absorption energy which accounts for the neutral interaction forces was suggested by de Boer:[105]

$$h\nu = (2A_m - 1)\frac{e^2}{r} + E_X - I_{Me} - \psi_{\text{pol}} - \Omega_X - \Omega_{Me},$$

where $(2A_m - 1)e^2/r$ is the work necessary to remove two adjacent charges against the electrostatic lattice energy, ψ_{pol} is the gain in energy due to the polarization of the surrounding ions, Ω_X is the absorption energy of the halogen atom in the lattice, and Ω_{Me} that of the metal atom formed in the lattice. de Boer showed that with certain assumptions for calculating the additional terms, a fair approximation was possible to the observed values of the first long-wave band.

Quantum Mechanics and the Formation of the Latent Image

As a result of the introduction of quantum mechanics, it became possible to elucidate many previously unexplained properties of solids, and it was natural that the latent-image problem should be similarly examined. The first attempt to correlate it with the concepts of quantum mechanics was made by Webb.[106] Following an earlier suggestion by Gurney[107] as to the origin of the coloration produced by ultraviolet light in alkali halide crystals, Webb assumed that the photographic latent image consists of one or more electrons trapped in discrete energy states around an irregularity in the silver bromide crystal lattice. The photoconductance property of silver bromide was used to explain how light absorption at random points all over the crystal can give rise to the latent image in discrete points. Quantum mechanics had given the first clear explanation of how the absorption of light produces freely mobile electrons in an insulating crystal. The transfer of light action through the photographic grain was attributed to these freely moving electrons. In this way, quantum mechanics explained the transfer of energy through the crystal and the relation of this to the photoconductance effect, and it provided a reasonable explanation for the Herschel effect and optical sensitization by dyes. It appeared that this new view of the behavior of electrons in solids contained elements of fundamental importance for the solution of the latent-image problem. However, outstanding difficulties still remained, the chief of which, perhaps, was that of reconciling the concept of the latent image as composed of electrons trapped in discrete states with the alternative view that it is composed of a small speck of silver.

The Gurney-Mott Theory

Gurney and Mott[108] proposed a definite theory of the latent-image process. This theory successfully combined the quantum mechanical concept of the primary process with a detailed picture of the subsequent reactions, based on recent experimental evidence of the silver halide structure. The new assumption of electrolytic migration of silver ions to discrete points in the crystal completed the mechanism for the concentration speck theory.

The formation of silver nuclei as a result of the absorption of light involves a consideration of the photoconductivity and electrolytic conductivity of silver bromide. From the principles of quantum mechanics, the increase in conductivity accompanying the absorption of light can be interpreted in terms of the zone theory of solids.[106] According to this view, the electronic energy spectrum of an insulating crystal such as silver bromide consists of a structure composed of bands of allowed energy levels separated by disallowed zones. In general, a different band structure would exist for each direction through the crystal, but for simplicity the present discussion may be limited to the one-dimensional case. The explanation of the property of insulation on this basis is that the lowest unfilled band of electronic energy levels is separated by a wide energy gap from the highest filled band. The photoconductance effect can be explained by the properties of these bands. In Figure 63 is shown a schematic diagram of two such energy bands for the silver bromide crystal. The upper, *S*, band may be regarded as associated with the silver ion lattice and is made up of the valence levels of all the silver atoms; an electron in this band would be shared by all the silver ions of the lattice. The lower, *P*, band of levels is associated with the bromide ions. In the normal state of the crystal, the *S* band contains no electrons, while the *P* band is filled with them, so that there is no possibility of electron conduction and the electrons cannot change their energy states under the action of an applied electric field. If, however, an electron were placed in the crystal with its energy state in the *S* band, it would behave like a free conduction electron in a metal, since it would have an abundance of adjacent energy states to transfer to under the influence of an electric field. Photoconductance in such a

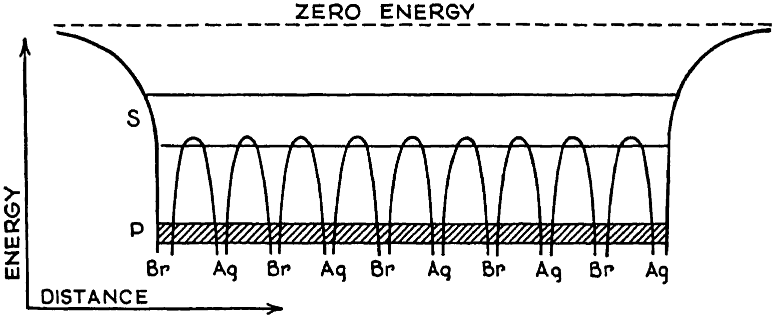

FIG. 63. Energy levels in silver bromide.

crystal is attributed to electrons in the lower band having their energy raised by absorption of light into the conductance band of the crystal, where they give rise to electronic conduction.

The photoconductance effect in silver halide crystals has been studied experimentally mainly by Pohl and his co-workers in Göttingen. The crystal is set up between electrodes with a known potential across them and the total current through the crystal measured during illumination. A voltage-current curve obtained by Lehfeldt[109] for silver bromide under constant illumination is shown in Figure 64. The curve starts to rise linearly with the voltage and then asymptotically approaches a maximum saturation value at high voltage. The explanation of this behavior is that the contribution to the electric current by each electron released by light depends upon the fractional distance between electrodes traveled by the electron before it comes to rest. The horizontal part of the curve is attributed to the fact that, at high voltages, electrons released by light are pulled all the way to the positive electrode, thereby producing saturation. At lower voltages, however, the electrons must be caught in some manner before reaching the electrode. That the electrons do not recombine with their parent bromine atoms is shown by the fact that the photocurrent increases as the first power of the intensity of the exposing light instead of the square root of the intensity, as would be required if recombination took place. It appears, therefore, that the electrons are caught in other ways, for which there is experimental evidence. Lehfeldt[109] and Hecht,[110] using silver halide crystals, showed that crystals containing colloidal particles of silver require higher electric fields for saturation. These experiments have been interpreted to mean that colloidal silver specks can act as traps to cut down the average distance traveled by electrons. This can be understood from the energy-level diagram of the metal and silver salt.

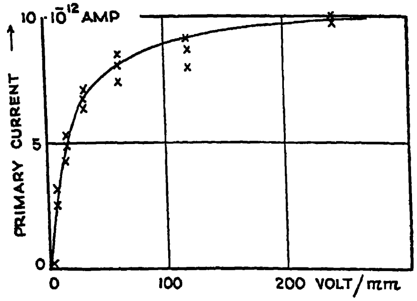

FIG. 64. Voltage-current curve for silver bromide under constant illumination

As already stated, the energy of a free electron in silver bromide lies in the upper conduction band. Gurney and Mott[108] point out that if the lowest energy level of this band lies above the highest filled conduction levels of the metal, as shown in Figure 65, an electron passing from the silver bromide to the metal descends through a potential step ΔE and is trapped.

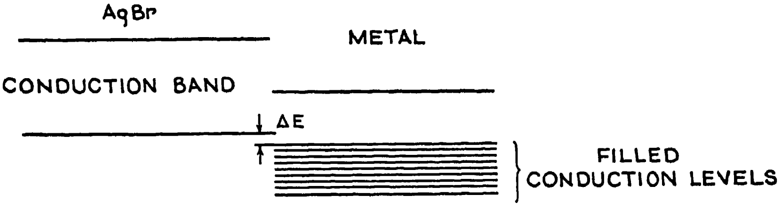

FIG. 65. Conduction levels in silver bromide.

The other property of silver bromide essential to the Gurney-Mott theory of the latent image is that of conductivity by ionic migration. Measurements of ionic conductivity of the silver halides have been carried out by a number of investigators, and it is well known that they exhibit relatively large conductivity even at room temperature. Tubandt[111] and his co-workers showed that the conductivity of the silver halides is due principally to the movement of the silver ions. The conductivity, λ, varies rapidly with temperature, in accordance with the law

$$\lambda = Ae^{-\epsilon/kT};$$

and from measurements by Lehfeldt,[112] the conductivity of silver bromide at room temperature amounts to approximately 10^{-8} ohm^{-1} cm^{-1}. It was not clear at first how silver ions could move through the crystal lattice as readily as indicated by the magnitude of the observed currents. The first satisfactory explanation of it was given by Frenkel[113] and has subsequently been worked out more fully by Jost,[114] Koch, Wagner, Schottky,[115] and others. According to this, at any temperature, T, a certain percentage of the silver ions are displaced from their regular lattice positions and pushed into interstitial positions. This is shown in Figure 66. The ionic conductivity of the silver halides is due to the movement of these interstitial silver ions and that of the vacant positions left in the lattice. That the silver ions, and not the bromine ions, are pushed into the interstitial positions is attributed to the smaller size of the silver ions. The interstitial ions are supposed to move either to other interstitial positions or those left vacant by the other ions, and may be regarded as forming within the crystal a gas of ions moving with thermal energies.

The Gurney-Mott theory may be applied to the direct print-out effect, that is, the photodecomposition of silver bromide on excessive exposure to light. As has already been said, the photo-equivalence principle holds for this process. The silver formed in this case is always found in coherent specks, whereas it is fairly certain that the light producing the silver is absorbed over the whole surface of the silver halide grain. Gurney and Mott postulate that, providing a minute amount of metallic silver is present in the grain initially, electrons liberated by light will become trapped on these specks and charge them negatively. They assume further that the electrostatic field set up in the grain by these negatively charged specks attracts the mobile interstitial silver ions and causes them to migrate to the speck. When these ions reach the speck, they neutralize the electrons already present and form silver atoms. Thus, the mechanism proposed affords a means whereby a speck of silver initially present can grow by one atom of silver for each light quantum absorbed. Furthermore, this theory shows how it is possible for light absorbed at random points on the grain to produce silver atoms only at certain discrete points.

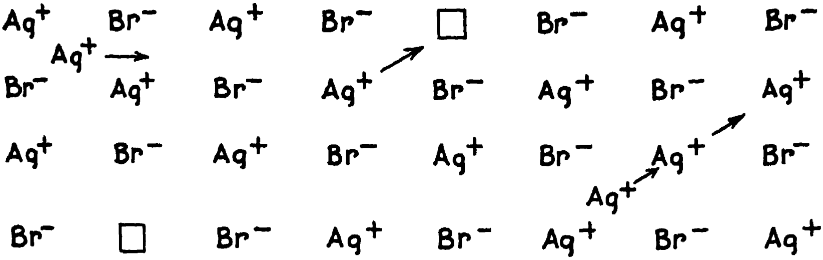
Ag+ Br− Ag+ Br− □ Br− Ag+ Br−
Ag+
Br− Ag+ Br− Ag+ Br− Ag+ Br− Ag+
Ag+ Br− Ag+ Br− Ag+ Br− Ag+ Br−
Ag+
Br− □ Br− Ag+ Br− Ag+ Br− Ag+

FIG. 66. Interstitial ions in the silver bromide lattice.

This description applies to the direct photodecomposition of silver bromide. For the latent image, the function of the concentration specks in controlling sensitivity must be explained.

Gurney and Mott assume that the silver sulfide specks discovered by Sheppard can play the role of electron traps in the same way as colloidal silver specks. Thus, the negatively charged silver sulfide specks attract the silver ions and act as nuclei for the initial growth of silver specks.

This theory of latent-image formation has many points in its favor. Fundamentally, it rests on well-established principles of atomic physics, and the mechanism proposed to account for the latent-image formation depends upon properties of silver halide that can be measured macroscopically in large single crystals. The theory has furnished an explanation of a number of features previously obscure. Furthermore, it accounts for the principal auxiliary effects connected with the latent-image process, such as reciprocity law failure and the Herschel effect, which are discussed later.

The strongest support for the Gurney-Mott theory of latent-image formation has been obtained from experiments at low temperature, such as those carried out by Berg and Mendelssohn,[116] Webb and Evans,[117] and Meidinger.[118] Some results obtained by Webb and Evans are presented in Figure 67. The characteristic curves *A* and *B* shown in the upper left-hand quadrant are for exposures made at room temperature and liquid-air temperature, respectively. The large drop in the photographic effect at the lower temperature is to be noted. The curves in the other three quadrants show the results of two series of interrupted exposures, both of which were made at liquid-air temperature. In the *A* series, the emulsion was warmed to room temperature for a brief interval during the dark period between exposures, while in the *B* series the emulsion was maintained at the low temperature during the dark periods. The *B* curves show that no effect is produced by interrupting the exposures made at liquid-air temperature provided the low temperature is maintained during the dark periods. The *A* series of curves, on the other hand, show that for exposures made in the same way, a marked effect is introduced by warming the emulsion to room temperature in the dark intervals following the exposures. It may be seen, further, that the effect is enhanced by increasing the number of subdivisions of the exposure and, accordingly, the number of warming periods. The experiments demonstrate that an action important in latent-image formation occurs during the warm periods between exposures.

According to the Gurney-Mott theory, the latent-image formation consists of two parts: (1) a primary process, in which electrons are released in the crystals and trapped by the sensi-

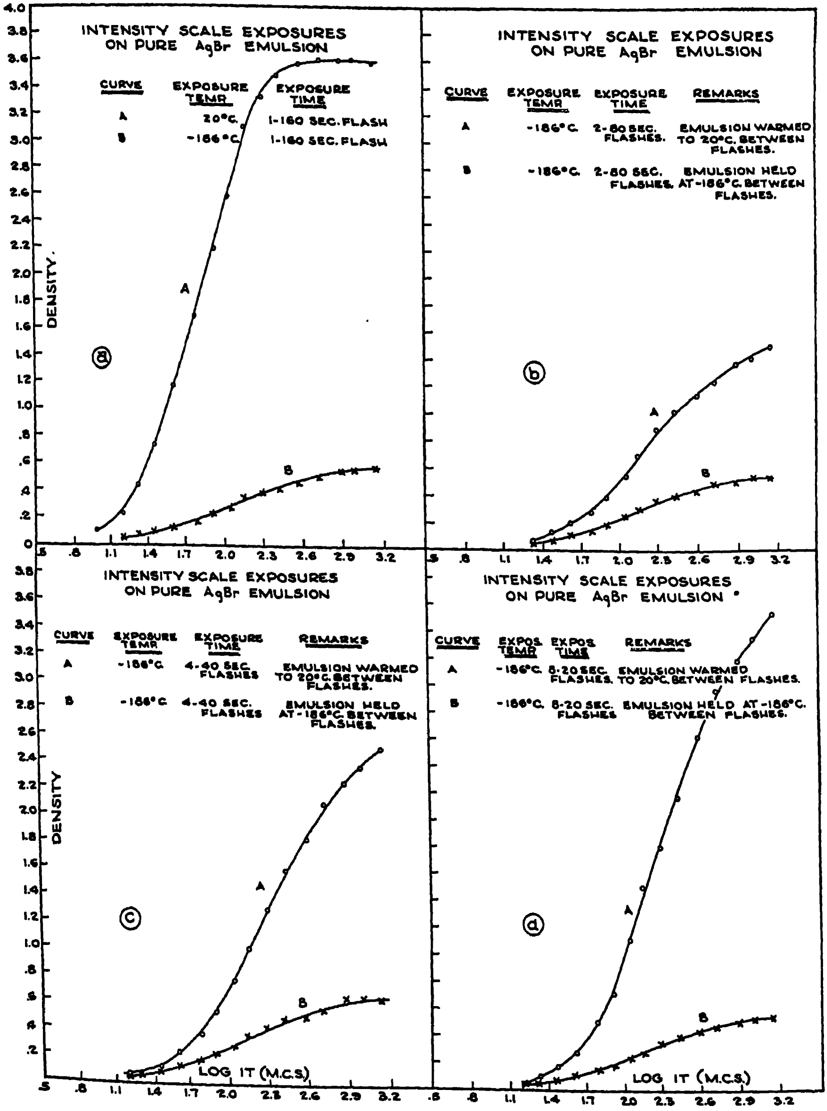

FIG. 67. Characteristic curves as influenced by temperature.

tivity specks; and (2) a secondary process, in which there is an electrolytic migration of silver ions to the negatively charged sensitivity specks. The former is an electronic process and has been shown by experiment to be unaffected by temperature down to −186° C. The secondary process, however, consisting of ionic conductivity, is known to be very dependent upon temperature. Both the number of interstitial ions and their mobility are dependent upon temperature, and at the temperature of liquid air it may be considered that the mobility of silver ions is zero for the photographic process. At this temperature, however, it must be supposed that one electron is released for each quantum of light absorbed by the silver bromide. At the temperature −186° C., there being no ionic conductivity, the electrons placed on the speck cannot be neutralized. Consequently, a sensitivity speck upon acquiring a few electrons becomes so highly charged that it repels further electrons. Under these conditions, some of the electrons liberated by light are repelled and lost for the latent-image process. Formerly, it was thought that these electrons would recombine with the parent bromine atoms. However, evidence [81] was presented in connection with the distribution of the latent image to show that most of these electrons become trapped at internal irregularities and form nuclei which are unavailable to the developer. This accounts for the large drop in density at the low temperature, as shown in Figure 67. If an exposure is given in installments and a warming period allowed after each installment with the same amount of light energy, a greater photographic effect is obtained than without warming periods. Furthermore, the curves show that the photographic effect increases with the *number* of interruptions and warming periods. According to the Gurney-Mott theory, the first exposure leads to the trapping of several electrons on a sensitivity speck. The emulsion being at liquid-air temperature, no silver ions can reach the speck to neutralize the charge due to the electrons. The warming of the emulsion during the dark period following the exposure, however, permits ionic movement and neutralization of the speck. A subsequent exposure and warming period causes the above chain of events to be repeated. As a given exposure is subdivided into a greater number of installments, the charge added to the speck during each exposure decreases. Since, for smaller unneutralized charges, fewer electrons are repelled from the speck, the photographic efficiency should increase with the number of exposure installments accompanied by warming periods. Accordingly, the experimental results presented in Figure 67 show that the primary and secondary processes postulated by Gurney and Mott for the formation of the latent image can be separated. The primary process occurs practically instantaneously even at liquid-air temperature, while the secondary process occurs only after the emulsion is warmed to well above liquid-air temperature.

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CHAPTER V

THE RELATION BETWEEN THE EXPOSURE GIVEN TO A LIGHT-SENSITIVE LAYER AND THE DENSITY OBTAINED AFTER DEVELOPMENT

The discussion of the action of light upon the silver halide grains has dealt up to the present point chiefly with the formation of the latent image in the individual grains. In practice, however, exposures are made upon emulsion coatings containing many grains and, usually, many layers of grains. The response of such multilayer coatings to exposure followed by development is of the greatest importance in the theory of photography and has been studied intensively during the last fifty years. The expression of the relation between the exposure and the silver deposit as a mathematical formula, which is the equation of the characteristic curve, has been attempted by a number of workers. The equations which have been proposed have sometimes been empirical, but, more generally, they have been based upon certain definite assumptions as to the action of light upon the sensitive layer.

The first photographic investigator to make quantitative measurements of the relation between the transparency of the image and the exposure was Abney,[1] who gave plates a graduated series of exposures, measured the transparency of the deposits obtained after development, and plotted curves showing the relation between the transparency and the exposure.

In his paper entitled "Photography and the Law of Error," in the *Journal of the Camera Club*, Abney suggested that the relation between the transparency, T, and the exposure, It or E, might be represented by the equation

$$T = e^{-u(\log It/i)^2} \tag{1}$$

This may be translated into the nomenclature introduced by Hurter and Driffield as:

$$D = K\left(\log \frac{E}{i}\right)^2, \quad \text{where} \quad D = \log \frac{1}{T},$$

and K and i are empirical constants. This equation fits only the lower part of the curve with any degree of approximation.

In 1890, F. Hurter and V. C. Driffield published in the *Journal of the Society of Chemical Industry* a paper[2] entitled "Photochemical Investigations," in which they put forth an experimental method of determining the characteristics of a photographic layer and a nomenclature for its optical properties which has since been generally adopted.

Hurter was a physical chemist who was chief chemist of the United Alkali Company, and Driffield was an engineer in the same firm. Driffield was keenly interested in photography and wrote:

> "In 1876 I induced Dr. Hurter to take up Photography as a recreation, but to a mind accustomed like his to methods of scientific precision, it became intolerable to practise an art which—at that time—was so entirely governed by rule-of-thumb, and of which the fundamental principles were so little understood. Five years' intimate acquaintance with Dr. Hurter and experience of his methods had deeply impressed me with his skill as an investigator, and, when it was agreed that we should jointly undertake an investigation with the object of rendering Photography a quantitative science, it was with a keen appreciation of my privilege that I joined Dr. Hurter as his collaborator."[3]

At the beginning of their work, the collodion process of photography was generally used, but it was being supplanted by the gelatin dry plate. Hurter and Driffield felt very strongly the necessity for some method of estimating the correct exposure to be given in the camera. To do this, they constructed an actinometer which enabled them to measure the variation in the intensity of sunlight throughout the day. They then constructed tables of intensity, which were embodied in an exposure calculator, which they called the *actinograph*, adapted to calculate the exposure from a number of factors, including the time of day and year, the weather, the subject photographed, etc. To determine the sensitivity of the plates which they used, they began a series of investigations which were published in the paper mentioned above. They first investigated the relation between the mass of silver produced after development and the exposure which had been given. Since the mass of silver is difficult to measure chemically, they studied the relation between the light transmitted by the silver deposit and the mass of silver per unit area.

It is well known that, for a dye or absorbing pigment and for monochromatic light, the logarithm of $1/T$ is proportional to the mass of the material present. This is generally known as *Beer's law,* and it follows from Lambert's law that if the thickness of an absorbing medium increases in arithmetical progression, the light transmitted decreases in geometrical progression. This law was actually stated by Bouguer[4] some thirty years before Lambert restated it. If a sheet of absorbing material is held in the path of a beam of light, the brightness will always appear diminished to the same extent for the particular piece of material, regardless of the brightness of the light. Thus, if the beam is diminished to a quarter, interposition of a second piece of the material will reduce the remaining beam, in the same manner, to a quarter of the new value, or one-sixteenth of the original. A third piece will reduce it to a sixty-fourth, and so on. If n equal layers are employed, each reducing the light to a fraction $1/m$, the intensity of the beam through n layers will be $(1/m)^n$ of the original. In place of a number of layers, the concentration of absorbing pigment may be increased in a single layer. Thus, if I_0 is the intensity of the original beam of light, I the intensity after penetration through the layer of pigment, and A the concentration of the pigment per unit area,

$$I/I_0 = e^{-kA}. \tag{2}$$

I/I_0 is termed the transparency, T. Hurter and Driffield termed $1/T$, that is, I_0/I, the opacity, 0; and using common logarithms instead of natural logarithms,

$$10^D = I_0/I = 1/T = 0 \quad \text{and} \quad D = \log_{10} 0,$$

D being termed by Hurter and Driffield the *density,** so that

$$D = \log_{10} 0 = \log_{10} 1/T. \tag{3}$$

It is seen that a density of unity corresponds to a transmission of 1/10 of the incident light; a density of 2, to the transmission of 1/100, etc.

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* The German term used for density is *Schwärzung.* This is frequently mistranslated as *blackening.*

Hurter and Driffield concluded from their experimental work that the density is proportional to the mass of silver per unit area; and this mass in grams per square centimeter, corresponding to a density of 1.0, is known as the *photometric equivalent, P.* This relation between the density and the mass of silver was confirmed by other workers, but later work has shown that the photometric equivalent varies with the size and nature of the silver grains forming the deposit. This subject is discussed later, p. 226. For the present, it is sufficient to assume that both the optical density and the mass of silver, if necessary, can be measured with considerable accuracy.

Continuing their work, Hurter and Driffield gave photographic plates a series of exposures increasing geometrically, developed the plates, and measured the density. They found that, through a very considerable range of exposures, the density increases arithmetically as the exposure increases geometrically; that is, the density is proportional to the logarithm of the exposure. Extending the work further, they found that the relation between the density and the logarithm of exposure, which they termed the *characteristic curve,* is only a straight line over its central portion; and the simple diagram in Figure 68 shows the general shape of the curve, which falls into three portions, each

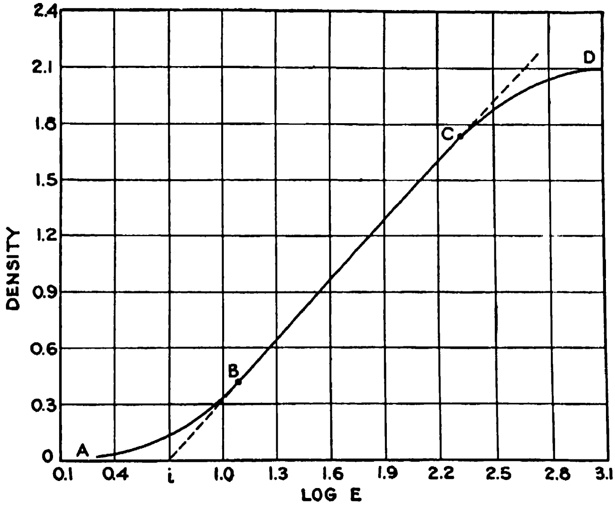

FIG. 68. Characteristic *D* log *E* curve.

of them merging imperceptibly into the next. There is, first, an induction period, and then the sensitive layer builds up density nearly linearly with exposure until the main portion of the curve is reached, where the density increases as the logarithm of the exposure. Then, with high exposures, the density ceases to increase as rapidly as the logarithm of the exposure until, finally, further exposure gives little or no increase in density. Still greater exposures, perhaps a million times more than that required to give the first perceptible density, cause reversal, and continued light action diminishes the density obtained upon development.

Hurter and Driffield extrapolated the straight-line portion of the curve to the exposure axis and termed the exposure corresponding to the point where it reached the axis the *inertia* (i) of the material. They used the reciprocal of the inertia as a measure of the sensitivity of the material and applied it to the calculation of exposure by means of the actinograph. As a result of many experiments, they found that for most emulsions, using developers in which there was no bromide present, the points of intersection of the extrapolated straight lines with the exposure axis did not change with the time of development or, within limits, with the composition of the developer. Thus, for the straight-line portion,

$$D = \gamma(\log E - \log i), \tag{4}$$

where i (the inertia) is expressed in exposure units and γ is the slope of the curve. The steepness of the slope increased with development (being zero with no development); hence, γ was termed the *development factor*. For fuller details concerning γ and development, the reader is referred to Chapter XI. The equation $D = \gamma(\log E - \log i)$ was found to hold for only a limited portion of the curve and had, apparently, no fundamental physical basis.

Hurter and Driffield then set out to deduce a mathematical expression for the whole extent of the curve, in the hope that it would reveal a simple law for the action of light. They made the basic assumption that all the material in a photographic layer is equally sensitive but that not all of it is favorably situated for exposure. The top layer receives light unimpaired and is affected first. Layers below the surface receive light which has been weakened by passage through the upper layers and would thus exhibit an apparent sensitivity diminishing with depth. They pointed out that when light of intensity I strikes the emulsion, the fraction α is reflected, and $I(1 - \alpha)$ penetrates the surface. If, at a particular moment, x particles of silver bromide per unit area are already changed, the transparency with respect to these is e^{-kx}. From the light admitted by this transparency, there should be deducted that which passes all the grains, the difference being the light absorbed by the material. The transparency of all the silver halide particles, a, in unit area is e^{-ka}, so that the light doing useful work is

$$I(1 - \alpha)(e^{-kx} - e^{-ka}). \tag{5}$$

From this result, Hurter and Driffield derived a differential equation for the rate of change of the halide particles exposed to light and integrated this to give a relation between the density of the developed image and the exposure, introducing as constants the opacity of the unexposed material, 0, and the γ of the developed image. The equation obtained was:

$$D = \gamma \log_e \left[0 - (0 - 1)\beta^{\frac{E}{i}}\right] \tag{6}$$

where

$$\log_e \beta = - \frac{1}{0}.$$

The assumptions made by Hurter and Driffield do not appear to be justified, so that their final equation is not satisfactory as a representation of the action of light on the emulsion layer.

Much later (1921), Helmick[5] modified Hurter and Driffield's equation by adding a group of parameters, including a series of powers of the logarithm of the exposure, and thus made it possible to obtain a better fit to the experimental results.

During the discussion of Hurter and Driffield's classical paper, which continued for some years, Elder[6] proposed a very simple formula analogous to the law of mass action. According to this law, first formulated by Guldberg and Waage, the velocity of a homogeneous chemical reaction is proportional to the concentration of the substances participating in the reaction, thus:

$$\frac{dC_x}{dt} = K(C_A - C_x) \tag{7}$$

and

$$C_x = C_A(1 - e^{-kt}), \tag{8}$$

where C_A is the initial concentration of the material, and C_x the concentration at any time, t. Thus, Elder wrote:

$$dn = KI(N - n)dt, \tag{9}$$

where N is the total number of grains which can be exposed and developed, n is the number changed at any time, t, and I is the intensity of light. Since N is proportional to D_m, the maximum density obtainable, this integrates to

$$D = D_m(1 - e^{-kE}), \tag{10}$$

where $E = It$. This formula fits the experimental data only to a very limited extent, because it disregards numerous important factors in the exposure of emulsion layers, notably the thickness of the multigrain layer and the consequent graduated absorption of light. Channon[7] suggested a more complicated formula based also on considerations derived from the law of mass action but involving the absorption of light in the multigrain layer.

Ross re-examined these equations in his monograph[8] and developed a new formula based on conservative assumptions. These were:

1. All the grains in an emulsion are divisible into n groups, each group as a whole obeying the mass action law.
2. The amount of silver in each group of grains is the same.
3. The sensitivity factors (r) of the groups can be arranged in geometrical progression. This takes account of the factors of (*a*) the true sensitivity difference and (*b*) the apparent sensitivity difference due to the thickness of the emulsion.

It is seen that Ross did not take into account explicitly the effect of penetration of light into the emulsion, but this effect was implicit in his analysis as an apparent variation in grain sensitivity superimposed upon the inherent sensitivity distribution curve.

On these assumptions, the equation connecting density with exposure can easily be derived. Calling D_m the maximum density (for infinite exposure); s, the sensitivity factor; r, the common ratio of the sensitivities of the various groups; the equation becomes

$$D = D_m\left(1 - \frac{1}{n}\sum_{s=0}^{s=n-1} e^{-kr^sIt}\right). \qquad (11)$$

Ross assigned a value to r of 1/2 and of $D_m = 5$ and then calculated the shape of curves for values of n varying from one for single-layer coatings to 10 for thick multilayer coatings. While the curves from Ross' equation are a closer approximation to the experimental results than those obtained from the earlier equations, a number of factors are still unaccounted for, notably the variation in sensitivity among grains, even in single layers.

Blair and Leighton[9] assume that the formation of the latent image is a reversible process; that is, during the action of light, not only are grains made developable, but some of these grains lose their developability; and that this action starts from the very beginning of exposure. With little exposure, the first process predominates, and the density produced after development increases. As the exposure is increased, the reverse process takes place; the increase of density diminishes and, finally, reversal begins, and with further increase of exposure, the developed density decreases. Blair and Leighton thus assume that (1) the formation of the latent image is the result of chemical action; (2) two processes occur during the action of light, the first forming the latent image and the second destroying it; (3) the first reaction is autocatalytic; the silver formed in the reaction increases its velocity; (4) the velocity of the first reaction follows the law of mass action; (5) the velocity of the reverse reaction is a function of the mass of the latent image already produced.

These assumptions are in general agreement with observed facts; and the reverse reaction, leading to solarization, is well known to occur. But Blair and Leighton assume that the reversal process begins at once, simultaneously with the direct process. The theory of the autocatalytic effect of the latent image on direct exposure is based on the known sensitizing action of colloidal metallic silver, on the action of a brief preliminary exposure, which is often stated to increase the sensitivity of an emulsion, and on the form of the characteristic curve.

Following these assumptions, the differential equation (12) expresses the formation of the latent image in a general form:

$$\frac{dD}{dt} = f_1(D) \cdot f_2(D_\mu - D) - f_3(D). \qquad (12)$$

In this, $f_1(D)$ expresses the autocatalytic action on the direct process; $f_2(D_\mu - D)$ gives the relationship between the direct reaction and the number of still-unchanged grains, since the difference $D_\mu - D$ between the maximum optical density and the optical density at a given moment is proportional to this number; finally, $f_3(D)$ expresses the relation for the reversal process. Blair and Leighton assume a simple relationship for the function f_2 and f_3; that is, they consider the law of mass action to be correct. However, they assume that the autocatalytic effect is proportional to $\sqrt{D}$. Therefore, equation 12 may be written in the following form:

$$\frac{dD}{dt} = K_1(D_\mu - D)\sqrt{D} - K_2D. \qquad (13)$$

Taking points on the D, t curve where maximum density has been attained and, therefore, $dD/dt = 0$, and using experimentally determined values of D_μ and D, the ratio of the constants K_1/K_2 can be obtained. By using this ratio along with experimental values of dD/dt and D for other points on the curve, values of K_1 and K_2 separately are obtained.

Equation 13 can be integrated to give:

$$e^{K_1t\sqrt{\left(\frac{K_2}{2K_1}\right)^2+D_\mu}\cdot C} = \frac{\sqrt{\left(\frac{K_2}{2K_1}\right)^2 + D_\mu} + \sqrt{D} + \frac{K_2}{2K_1}}{\sqrt{\left(\frac{K_2}{2K_1}\right)^2 - D_\mu} - \sqrt{D} - \frac{K_2}{2K_1}}, \qquad (14)$$

where C is the constant of integration. The integrated equation is rather complicated but, by careful choice of constants, it has been shown capable of representing the experimental curves fairly accurately. A curve plotted from this equation and compared with experimental data is shown in Figure 69. Considering the number of postulates made in deriving the equation and the number of constants involved, it cannot be said that this equation lends itself to a simple interpretation of the photographic process.

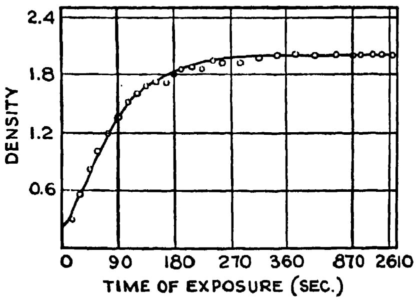

FIG. 69. The relation between density and exposure according to Blair and Leighton.

Chapuis,[10] in an analysis of the characteristic equations proposed by others, starts from the assumption that the law of formation of photographic density is analogous to the law relating the pressure to the volume of an ideal gas. There does not seem to be any real justification for this analogy except that it gives a simple physical basis for the computation of an equation. Following the analogy with the equation

$$(p + p_0)v = p_0v_0, \tag{15}$$

Chapuis derives as his simplest equation for a single-grain layer

$$D = D_m \frac{E}{E + E_0}. \tag{16}$$

This is then modified to allow for the absorption in a thick emulsion layer, for the depression of density produced by the presence of bromide in the developing solution, and for the insufficient permeability of the lower emulsion layers during development. The final equation was tested by Chapuis on three types of emulsion, and reasonably satisfactory agreement was obtained.

In practice, the most important variation in the characteristic curves of different photographic materials is in the toe of the curve. This portion of the curve was discussed by Hurter and Driffield, who found that in it a linear relationship existed between exposure and the density:

$$D = kE. \tag{17}$$

Luther [11] suggested that the shape of the underexposed portion of the curve could be demonstrated most clearly by plotting densities against ($\log E - \log i$) instead of against $\log E$. If the different emulsions are developed to the same value of γ, the straight-line portions of the curves are coincident, and differences in other portions of the curve are easily seen. Thus, in Figure 70, three curves are shown to have the same straight-line portion but to differ in the toe portions. These correspond to (1) a portrait plate, (2) a medium plate, and (3) a contrast plate used for reproduction work. Luther points out that the simplest assumption which can be made as to the differences in the toe portions of the curves is that the triangles between the abscissa, the curve, and the produced straight line are geometrically similar. Then it would be possible to convert any one curve into any other by multiplying D and $\log E/i$ by the same factor. From measurements of the curves of forty different materials, Luther found that the toe portions of all characteristic curves of the same γ are geometrically similar, so that a single constant is sufficient to express the shape, or rather the extent, of the toe portion of the characteristic curve. The equation for the toe portion of the curve is

$$D = \frac{\gamma}{h} f\left(\log \frac{E}{i} h\right), \tag{18}$$

where h is the factor characterizing the *hardness* of the emulsion. The higher the value of h, the shorter the toe. It follows that the slope of the characteristic curve at the exposure value corresponding to the inertia must be a constant fraction of γ, independent of γ and of the material. Luther found that the fraction is approximately one-half.

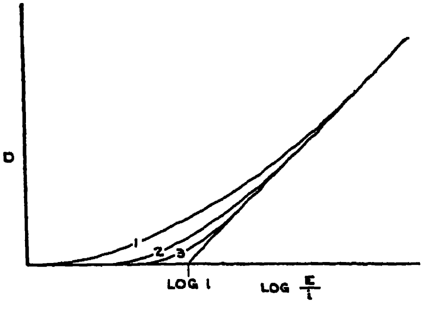

FIG. 70. The shape of the underexposed portion of the curve according to Luther.

Renwick[12] points out that Hurter and Driffield's expression requires modification and suggests the expression

$$D = kE - C \tag{19}$$

as representing the toe of the curve. The parameters of this equation, K and C, were determined by Bloch.[13]

The study of the effect of exposure by statistical methods, which has already been discussed (Chapter IV), led to the derivation of equations for the relation between exposure and density. These studies, starting with the work of Svedberg and of Slade and Higson,[14] suggest that the likelihood of a grain becoming developable after any particular exposure should be predictable from considerations of probability. The general probability may be expressed in the form

$$P = f(It); \tag{20}$$

but since the grains are dissimilar and can be grouped into a number of classes, the law has a different form for each class.

To eliminate class differences as much as possible, Slade and Higson used a very uniform emulsion which they spread upon glass in a single-grain layer. For the purpose of measurement, they made the inexact assumption that the grains were identical in size and quality. Their method was to count, under the microscope, the relative number of grains which were blackened by prolonged treatment with developer (to insure reduction of every affected grain) for different degrees of light exposure. The experiments resulted in two series of numbers, of which the following are typical. When they are plotted, one against the other, a curve is obtained analogous to the $D \log E$ curve of a multilayer emulsion.

Relative intensity of light, time of exposure being constant	*Percentage changed of grains originally present*
142.0	100 (approx.)
67.0	92 "
49.8	70.4
34.0	39.1
16.6	11.2
8.13	5.8
3.98	2.6
2.24	0.5

Slade and Higson argue that if the grains are identical in sensitivity and their developability depends upon the chance absorption of light quanta, the number of grains made developable in any small interval of time will be proportional to the number of grains remaining unchanged at that time. Let x of a grains be changed when exposed to light of intensity I for a time t. Then the fraction $a/(a - x)$ should vary as e^{kIt}; but they found that, at high intensities, $a/(a - x)$ varies linearly with I and at low intensities with I^2. When I was kept constant while the time of exposure was varied, the change of $a/(a - x)$ with t was not linear. From this, Slade and Higson conclude that light does not act in quanta.

The experiments of Slade and Higson are insufficient to give definite proof of their conclusions, and their deductions would be valid only if it were assumed that the grains are made developable by a single quantum of light absorbed.

Svedberg's [15] experimental method also consisted in the coating of plates with a single layer of grains, although Svedberg made no attempt to have the grains of a uniform size. By the experimental method described previously (Chapter IV, p. 145), he determined the average number of developable centers per grain:

$$v = \frac{k}{n}, \tag{21}$$

where k = total number of centers in the grains
and n = total number of grains.

He showed that the centers of developability obey Poisson's law of distribution. Then,

if x = number of developable grains of a certain size in a given area
and n = total number of grains of this size in this area,

$$\frac{x}{n} = 1 - e^{-v}, \quad \text{or} \quad \frac{x}{n} = 1 - e^{-k/n}, \tag{22}$$

which gives the fraction of the developable grains as a function of the number k of the centers produced on the grains; k and x vary with the exposure and with the size of the grains, whereas n is constant for a given size and area.

Svedberg's equation (22) gives a curve of the same shape as the characteristic curve, the shoulder being produced by the gradual exhaustion of the undeveloped grains and having exactly the same form as is given by Elder's equation:

$$D = D_m(1 - e^{-kE}). \tag{23}$$

Both of them show that the increase in the number of developed grains with increasing time of exposure is proportional to the number of undeveloped grains remaining. The derivation of the two equations is, however, different: Elder's differential equation deals with the silver bromide as a whole, while Svedberg's formula is a probability function derived from statistical considerations. Svedberg assumed that since the silver halide material of all the grains of the same emulsion should be uniform, the average number, v, of the developable centers per grain should be proportional to the area of the grains, a, or

$$v = ac, \tag{24}$$

where c depends upon the exposure. Svedberg tested this conclusion experimentally and considered that the average number of developable centers for a given area of a grain is fairly constant. However, later work by Toy[16] did not confirm this result. Thus, the ratio $v_2 : v_1$ of the average numbers of centers, v, for two sizes of classes, a_1 and a_2, was studied. According to Svedberg, this ratio should be independent of exposure; but Toy did not find this result, and a further study by Sheppard and his collaborators also showed that the larger grains have a disproportionately greater number of developable centers for their area.

It is seen that in all this work the relation between the developed density and the exposure to light is based upon assumptions as to the mechanism of exposure. The assumption most frequently employed in investigations of this type is that a fixed, minimum number of quanta are required for the production of a just developable latent image, this minimum number being assumed to be the same for every photographic grain. All theoretical analyses based on this fundamental assumption have led to the same conclusion, namely, that a very few quanta (1 to 4) are utilized by the photographic grain in the acquisition of a just developable latent image. Silberstein[17] is the author of such a theory of photographic exposure. He considers the silver halide grains as targets exposed to haphazard bombardment by a shower of "light-darts," or photons, each carrying a quantum of energy, and assumes the probability of an effective hit by a single photon to be proportional to the size (projective area), a, of the grain, *viz.*, ϵa, where ϵ is a small numerical fraction to be evaluated experimentally. If n is the total number, per unit area, of photons thrown upon the plate, then, under the assumption that a single quantum hit is sufficient for making a grain developable, the number k of grains, out of a total of N grains of size a, made developable is

$$k = N(1 - e^{-\epsilon a n}), \qquad (25)$$

with the probable error, $\pm 0.477\sqrt{2k(1 - k/N)}$. If two light quanta are required for developability, the term $e^{-\epsilon a n}$ in (25) must be multiplied by the factor $1 + \epsilon a n$; for three quanta, by the factor $1 + \epsilon a n + (1/2!)(\epsilon a n)^2$; and so on. A factor is also provided which takes care of the small but finite breadth of each size-class of grains.

A series of photomicrographic measurements was made by Trivelli and Righter[18] with single-layer coatings. Clumps of grains in these were found to behave like single grains, and the numerical results from this work were in fair agreement with Silberstein's formula, both as regards the dependence on size, a, and the exposure, which is proportional to n. Moreover, absolute energy measurements gave ϵ values ranging from 10^{-5} to 10^{-4}, of the same order as the efficient fraction of the area of a photoelectric potassium cell, as found by Elster and Geitel and Pohl and Pringsheim.

More accurate and more extensive photomicrographic studies by Trivelli disclosed a number of considerable discrepancies between the actual counts of grains and formula (25) or its first few amplifications.

It was then suggested by Silberstein and Trivelli[19] that while a photon of visible light may be too weak to make a grain developable, a single photon or quantum of X rays, which carries several thousand times as much energy, ought to be sufficient for this purpose. Experiments with X-ray exposures of different intensities and grain sizes (in 20 classes) ranging from 0.2 to nearly 6 μ^2 yielded results agreeing with formula (25).

The original formula has been modified by Silberstein and Trivelli [20] to cover the absorption of the incident light in multilayer coatings and also the distribution of the sizes of grains which occur in practical emulsions. Silberstein assumes that a grain becomes developable when, of the total quanta falling upon it, r quanta falling on a sensitive area of the grain ϵa are effective in producing photochemical decomposition, r being an integer and ϵ the small fraction corresponding to the "effective area" of the grain. He shows that for small values of exposure

$$D \propto E^r;$$

that is, *initially*, the density is proportional to the rth power of the exposure. The value of r can thus be deduced from the rate at which D increases with E. Inasmuch as values of r, other than very low ones, produce impossibly rapid increases of the density as the exposure is increased, this result leads to the conclusion that of the quanta falling on a grain, only a very few, from one to four, for example, are effective.

This conclusion should be considered in the light of its discussion by Webb,[21] who points out that the small value for r results from the assumption that all grains are equally sensitive. If each grain requires the same number of effective quanta to become developable, variations of sensitivity among grains must be accounted for by statistical fluctuations in the number of effective quanta received by different grains. The formula for calculating the fraction of developable grains by an exposure y (average number of quanta/grain) is the Poisson probability equation,

$$\frac{k}{N} = \sum_{n=r}^{n=\infty} \frac{e^{-y} y^n}{n!}, \tag{26}$$

where k/N is the fraction of grains rendered developable and r is the minimum number of quanta required to render a grain developable. A series of curves drawn from this equation is shown in Figure 71, in which it is seen that to obtain a theoretical curve with exposure latitude comparable with that observed in actual curves, a small value of r is required.

In a paper in which the problem of photographic exposure of an emulsion was treated by a graphical analysis, Webb [22] derived an equation for the density-exposure relationship based upon the alternative assumption that grains have varying sensitivities. This treatment deals with the quanta incident on the grain but can readily be put in terms of absorbed, or effective, quanta per grain if these quantities are proportional to the incident quanta. As in the work of Ross, Webb does not include explicitly the effect of absorption by the upper layers of the emulsion but lets this effect enter as an additional variation of sensitivity. Based on data from exposure-grain count experiments for single-grain layer plates, the following form of function was chosen to represent the variation of sensitivity among the emulsion grains,

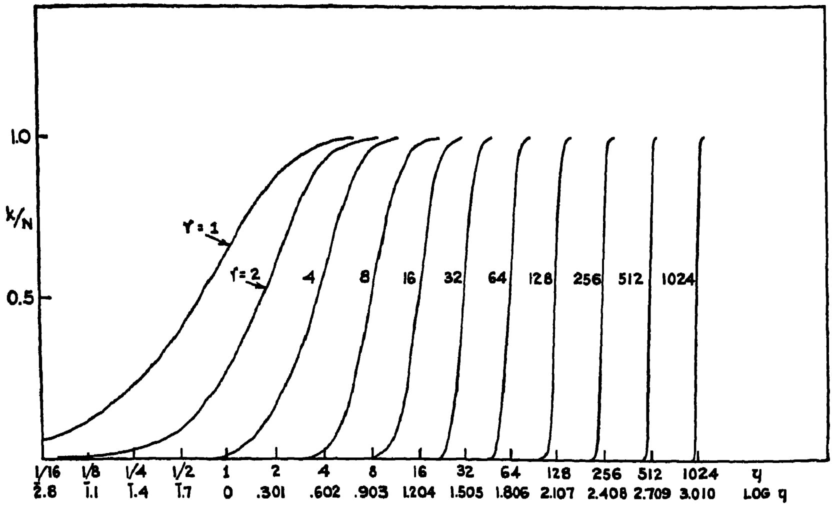

FIG. 71. Curves corresponding to different values of r in the Poisson probability equation.

$$z = f(x, y) = A_x e^{-k(\ln y - \ln \delta)^2}, \qquad (27)$$

which expresses, for the grains of size class x, the number of grains as a function of the sensitivity y. In this equation, A_x is an amplitude factor, which varies with size class in accordance with the grain size-frequency distribution of the emulsion. The variable y represents grain sensitivity measured in exposure required to render a grain developable, and δ is a constant corresponding to the most probable sensitivity value. The parameter

k determines the shape of the sensitivity distribution curve. The amplitude factor A_x can be written in terms of the size-frequency function $\phi(x)$ by means of the relation

$$\phi(x)dx = \left[A_x \int_0^\infty e^{-k(\ln y - \ln \delta)^2} dy\right] dx, \tag{28}$$

which expresses the fact that the number of grains of sensitivity values between the sizes x and $x + dx$ must equal the ordinate of the size-frequency curve. The total number of grains rendered developable by an exposure E per unit area of plate is obtained by integration of the volume under the surface

$$z = f(x, y) \tag{29}$$

between the limits $y = 0$ and $y = Ex$ and $x = 0$ to ∞. Substitution of the grain area-frequency function $\phi(x) \cdot x$ for the grain size-frequency function gives an expression for the total projective area of developable grains, a quantity directly related to density D. With this change, the equation finally obtained for density as a function of log exposure is:

$$D = \frac{D_m}{2} \int_0^\infty \left[1 + \frac{2}{\sqrt{\pi}} \int_0^{2.3\sqrt{k}\ln\frac{Ex}{Q}} e^{-\beta^2} d\beta\right] \phi(x) \cdot x dx, \tag{30}$$

in which D_m is the density for infinite exposure and Q (defined by the relation $\ln Q = \ln \delta + (1/2k)$) is the value of Ex for which one-half the grains of size x have become developable. The quantity k is the only arbitrarily adjustable parameter for bringing the theoretical and experimental curves into accord. This equation for the characteristic curve, containing, as it does, the probability integral and the grain area-frequency function for which a generally valid expression has not been obtained, cannot be integrated directly. Accordingly, the equation has to be solved by graphical means, which is a long and tedious process. The equation, however, has been tested for a number of widely differing types of emulsions and shown to give results in good agreement with experiment.

Equation (30) without the factor $\phi(x) \cdot x$ representing the grain size-frequency distribution is recognized as the probability integral. This integral had been employed by earlier workers to represent the characteristic curve. Lienau[23] refers to this equation in its integral form as the *law of the geometric mean.* His formula for the density-exposure relation is

$$D(E) = \frac{D_m}{\sqrt{2\pi}} \int_{-\infty}^{S} e^{-1/2\, S^2} dS, \tag{31}$$

where $D(E)$ is the density for the exposure E, D_m is the maximum attainable density, and S is related to E by the equation:

$$S = S_0 \log_e \frac{E - E_0}{E_g - E_0}, \tag{32}$$

in which S_0 and E_0 are constants and E_g is that value of E for which $D = D_m/2$. Lienau tested this equation by comparison with density-exposure curves for ordinary emulsions and found it to hold closely.

An equation very similar to the above is given by Houstoun.[24] This gives the relation between the fraction of developable grains and exposure and may be written

$$\frac{k}{N} = \int_{-\infty}^{\log E_e} e^{-\frac{\left(\log \frac{E}{E_0}\right)^2}{2\sigma^2}} \cdot d(\log E), \tag{33}$$

in which E_0 and σ are constants. Houstoun tested this equation by comparison with experimental exposure grain count data for a number of emulsions and found it capable of giving good agreement with the experimental data.

Evidence against the validity of the assumption that all grains have the same inherent sensitivity is given in a paper by Selwyn,[25] in which he attempts to fit the Poisson equation

$$\frac{k}{N} = \sum_{n=r}^{n=\infty} \frac{e^{-y} y^n}{n!} \tag{34}$$

to data obtained from exposure grain count experiments by Toy.[16] According to the Poisson equation, the curve with the minimum possible slope is obtained by setting r equal to one, which corresponds to the case of a grain being rendered developable by a single quantum. However, Selwyn shows that the data obtained by Toy on grains selected carefully for geometrical equality give characteristic curves with slopes substantially less than the theoretical minimum. Since fractions of a quantum are physically meaningless, the Poisson equation cannot fit the experimental curves in this case. It appears more likely, therefore, that nearly all the spread of Toy's curves along the exposure axis must be attributed to variations in sensitivity from grain to grain. It seems necessary to conclude that at least some cases exist in which all geometrically identical grains of an emulsion are not of equal sensitivity. This was maintained by Toy in the paper quoted.

In a later paper, Silberstein takes issue with the ideas put forth by Webb and Selwyn and derives a generalized expression for the characteristic curve, based on the application of formula (34) to grains of different sensitivity values, r. The quantity k/N represents the percentage of grains of sensitivity r acquiring a latent image, and y is the average exposure value per grain (all grains considered of the same size). Silberstein points out that the most general formula relating the number of developable grains to the exposure is obtainable on the assumption that the emulsion is made up of a great number of grain classes, each class having a different sensitivity value, r. He supposes that the numbers, r, of quanta required (in each case a minimum) by the grains extend over the whole range of positive integers, from $r = 1$ to $r = \infty$, and assumes the sensitivity distribution is represented by some function, $f(r)$. The fractional number of grains requiring one quantum is represented by $Nf(1)$; the fractional number requiring two quanta, by $Nf(2)$; and, in general, the fractional number of grains requiring r quanta, by $Nf(r)$, where the function (r) satisfies the normalizing condition

$$\sum_{r=1}^{r=\infty} f(r) = 1. \tag{35}$$

The expression for the fractional number of grains of all sensitivity classes rendered developable by an exposure y can then be written as

$$\frac{k}{N} = \sum_{r=1}^{r=\infty} f(r) \sum_{n=r}^{n=\infty} \frac{e^{-y}y^n}{n!}, \tag{36}$$

which corresponds to a superposition of the individual characteristic curves for the separate sensitivity classes.

Instead of working directly with equation (36) of the characteristic curve itself, which becomes exceedingly complicated, Silberstein makes use of the derivative equation. He obtains this by the addition of the slopes of the elementary curves for grains of differing sensitivity, r, where r varies in a manner specified by the function $f(r)$. He shows (but with certain restrictions on the form of $f(r)$) that any but small values of r (below about 10) lead to impossibly steep curves. The important point is the choice of the function $f(r)$ to specify the sensitivity distribution among the grains of the emulsion. In his analysis, Silberstein limits his treatment to a "reasonable form" of the function $f(r)$ and says:

> "Now, with any reasonable form of $f(r)$, the resultant $\bar{y}$ is not far off from the arithmetical mean or average of the partial inflection exposures $\bar{y}(r) = r$. . . ."

Thus, the exposure value of the inflection point $\bar{y}$ of the composite characteristic curve must agree approximately with the arithmetical mean of sensitivity values of the different grains of the emulsion. With the restriction of the choice of $f(r)$, the analysis and conclusions given by Silberstein [26] are undoubtedly correct; the shape of the experimental characteristic curves indicates that only small values of r are admissible. However, this depends upon the validity of the restriction placed on the choice of the form of the function $f(r)$.

In replying to the above paper by Silberstein, Webb [27] pointed out that the only form of the function $f(r)$ which permits large values of r is one in which the exposure of the inflection point y of the composite characteristic curve agrees more nearly with the geometrical mean of the sensitivities of the grains, and this type of function is excluded by Silberstein. Using a graphical method of analysis, Webb studied several different forms of the function $f(r)$ that would give curves of the generally correct shape. The plan of procedure is, in principle, the same as that employed by Silberstein except that the characteristic curves themselves instead of the derivative curves were studied. The functional forms studied included $f(r) = \alpha/r$ and $\alpha/r\, e^{-\gamma r}$, but the form which was found to give better agreement with experimental curves generally is

$$f(r) = \alpha e^{-k(\ln r - \ln r_0)^2}. \tag{37}$$

This functional form is identical with the sensitivity distribution function expressed by equation (27) by Webb and contained implicitly in the integral equations of Lienau and Houstoun. From equation (37), it is found that curves of the correct shape can be obtained only if r is allowed to vary over a range of values approximately equal to that of the exposure latitude of the emulsion.

de Langhe,[28] using statistical analysis, gives an equation for the characteristic curve of the photographic emulsion based on fundamental assumptions somewhat different from those made by other workers. He assumes that each absorbed quantum forms a packet of silver atoms of size η ($= 1, 2, 3$, or more), the value of η being constant for quanta of a given energy. It is supposed that these atom packets of one or more atoms add themselves to sensitivity centers pre-existent on the grain to form development nuclei. The most important feature of de Langhe's treatment is the assumption that not all the sensitivity centers require the addition of the same number of atom packets to become development nuclei. He supposes that there are distributed among all the photographic grains on a given area k_0 sensitivity centers requiring the addition of no packets (fog grains), k_1 sensitivity centers requiring the addition of one packet, k_2 sensitivity centers requiring the addition of two packets, k_3 sensitivity centers requiring the addition of three packets, and, in general, k_i sensitivity centers requiring the addition of i packets to become development nuclei. The value of i is supposed to terminate at some definite value, depending on the emulsion. The total number of atom packets per unit area formed by the exposure may be represented by N. Letting N_i represent the number of packets added to the sensitivity centers which require i packets, the probability W_r that one of the k_i sensitivity centers acquires r of the N_i packets is given by the formula

$$W_r = \frac{N_i}{r!(N_i - r)!} \frac{(k_i - 1)^{N_i - r}}{k_i^{N_i}}. \tag{38}$$

The probability that one of the k_i sensitivity centers acquires *at least* a number i of the N_i packets and, thus, becomes a development nucleus is

$$\frac{k_i'}{k_i} = \sum_{r=i}^{r=\infty} W_r, \tag{39}$$

where k_i' represents the sensitivity centers which have become developable.

The total number of development nuclei k' is obtained by a summation of the k_i' for all values of i from zero to s. Thus,

$$k' = \sum_{i=0}^{i=s} \sum_{r=i}^{r=\infty} k_i W_r. \tag{40}$$

The average number of development nuclei v per grain can be found by dividing the total number of nuclei k' by the number of grains n. The final formula obtained by de Langhe for the average number of development nuclei per grain is

$$v = \frac{k'}{n} = \sum_{i=0}^{i=s} \frac{k_i}{n}\left[1 - \left(\frac{k_i - 1}{k_i}\right)^{k_i\frac{N}{k}}\left(1 + \sum_{r=1}^{r=i-1} \omega_r\right)\right], \tag{41}$$

where

$$\omega_r = \frac{N_i!}{r!(N_i - r)!}\,\frac{1}{(k_i - 1)^r}\,.$$

If k_i is very large compared with unity, the approximation can be made that

$$\left(\frac{k_i - 1}{k_i}\right)^{k_i} \approx e^{-1}. \tag{42}$$

With this and other minor changes, equation 42 can be written

$$v = \frac{k_0}{n} + \frac{k - k_0}{n}\left(1 - e^{-\frac{N}{k}}\right) - e^{-\frac{N}{k}} \sum_{i=1}^{i=s}\left(\frac{k_i}{n} \sum_{r=1}^{r=i-1} \omega_r\right)\cdot \tag{43}$$

The number of developable grains is a simple function of v, the average number of nuclei per grain, as may be seen from the following consideration: The probability ω_r that one of the n grains acquires a number r of the k' development nuclei is given by a formula similar to (38); namely,

$$\omega_r = \frac{k'!}{r!(k' - r)!}\,\frac{(n - 1)^{k'-r}}{n^{k'}}\,. \tag{44}$$

The probability that a grain acquires *at least one* active nucleus, which is the condition necessary for its developability, is

$$\frac{x}{n} = 1 - \omega_0 = 1 - \left(\frac{n-1}{n}\right)^{k'}$$

and for large values of n may be written

$$\frac{x}{n} = 1 - e^{-\frac{k'}{n}} = (1 - e^{-v}). \tag{45}$$

The fraction of developable grains x/n as a function of the number of atom packets N (N = number of absorbed quanta for exposures to light) may be obtained from (45) and (43).

de Langhe's treatment allows somewhat more latitude in the shape of the characteristic curve than the methods of other workers by virtue of his assumption that the sensitivity centers have varying sensitivities. In this way, the grains effectively cover a somewhat wider range of sensitivities than would otherwise be the case. de Langhe's method does not allow a great variation in sensitivity among grains, however, because the sensitivity centers of varying sensitivity are assumed to be distributed uniformly among all the grains and, therefore, on the average, each grain has the same sensitivity.

The mathematical treatment given by de Langhe is valuable in that it gives a technique for dealing with the exposure problem if more than one sensitivity center exists on a grain and also if the centers have varying sensitivities. In this connection, an important feature is brought out in de Langhe's calculations: Computation of the mean number of development nuclei v as a function of the total number of sensitivity centers k shows that the curve for v passes through a definite maximum. This is in qualitative agreement with the fact, well known to emulsion makers, that there is an optimum point to which ripening of an emulsion can be carried, beyond which the sensitivity of the emulsion decreases. The ripening process presumably corresponds to the formation of sensitivity centers on the grain.

Up to this point, the equations for the characteristic curve have attempted to give the relation between density and exposure It on a photographic plate, omitting the effects of reciprocity law failure and the factor of wave length. It is well known that, because of reciprocity law failure, the shape of the characteristic curve depends upon whether the exposures are made by variation of the intensity or the time factor of exposure; and, furthermore, if the curve is on the intensity scale, the shape depends upon the time of the exposure (Chapter VI, p. 241). Also, the slope of the characteristic curve varies with wave length of the exposing radiation owing to variations in the absorption and scatter of light by the grains.

A generalized equation for the curve has been derived by van Kreveld,[29] taking account of the factors of wave length and exposure time, based on certain fundamental experimental relations that have been found to hold. While this equation contains several arbitrary functions of λ and t, which are still undetermined, it shows, nevertheless, how these functions must enter into any general equation of the characteristic curve which includes these factors. A derivation[30] of this general photographic density law is given below. (See also Chapters VI, p. 250 and XVIII, p. 687.)

As pointed out in the next chapter, the log It values necessary to produce a constant density plotted as a function of the exposure time can be expressed[31] by the equation

$$\log It = F_1(D, t) + F_2(D, \lambda). \tag{46}$$

Or, since the variations of log It occasioned by reciprocity law failure correspond to changes of log I alone, when the reciprocity curves are plotted as a function of time, this equation can be written in the form

$$\log I = F_1(D, t) + F_2(D, \lambda). \tag{47}$$

Further, the van Kreveld addition law[31b,31c,32] states that the photographic emulsion adds radiation in accordance with the law

$$\Sigma S(D, \lambda_n) i_{\lambda_n} t = 1, \tag{48}$$

in which i_{λ_n} represents the intensity of the component radiation of wave length λ_n in the mixed exposure and $S(D, \lambda_n)$ is the sensitivity of the emulsion expressed as the reciprocal of the energy of wave length λ_n required to produce a density D in time t. Stated in this way, equation (48) applies to the case of simultaneous addition of radiations. This equation has also been found [32] to hold for successive exposures to light of different wave lengths provided the intensities of illumination are adjusted to give equal photographic effects in equal times. In the case of simultaneous addition, the times of exposure to all components are the same and the intensities are additive, while in the case of successive addition, the effective intensities of all components are the same and the times are additive.

From experimental work carried out primarily to test the validity of the addition law (48) for successive exposures to different-colored radiation, it has been found [32] that the slopes of two intensity scale curves made to different wave lengths but having the same time of exposure bear a constant relationship to each other; that is,

$$\left[\frac{\partial(\log I)}{\partial D}\right]_{\lambda_1} \Big/ \left[\frac{\partial(\log I)}{\partial D}\right]_{\lambda_2} \tag{49}$$

is independent of density. The fundamental experimental facts expressed by equations (47) and (49) form the bases of the generalized equation of the characteristic curve given by van Kreveld. By substituting (47) in (49), it is found that

$$\frac{F_1'(D, t) + F_2'(D, \lambda_1)}{F_1'(D, t) + F_2'(D, \lambda_2)} \text{ is independent of } D, \tag{50}$$

which requires that

$$\begin{aligned} F_1'(D, t) &= \psi(D) f(t), \\ F_2'(D, \lambda) &= \psi(D)\phi(t). \end{aligned} \tag{51}$$

These equations can be integrated to give the generalized equation

$$D = F\left[\frac{\log I - \{f_1(t) + \phi_1(\lambda)\}}{\{f(t) + \phi(\lambda)\}}\right]. \tag{52}$$

This expresses the remarkable fact that the shape of the characteristic curve obtained by variation of the intensity factor of exposure, keeping the time constant, depends upon the time of exposure and the wave length of the exposing radiation only to the extent of a bodily shift along the log It axis by the amount $\{f_1(t) + \phi_1(\lambda)\}$ and a stretching in the same direction by the factor $\{f(t) + \phi(\lambda)\}$.

It is possible to interpret[29] the different terms of (52). The quantity $\phi_1(\lambda)$ is a wave-length factor which corresponds to the spectral sensitivity of the emulsion. The wave-length function $\phi(\lambda)$ gives the dependence of the steepness of the characteristic curve on wave length. This function depends upon the shielding effect of absorption and the turbidity and sensitization of the emulsion for the wave length in question. The functions $f_1(t)$ and $f(t)$ depend neither on the wave length nor the density and, therefore, must be considered characteristic of the fundamental photographic process.

THE PHOTOMETRIC EQUIVALENT

In all the work which has been done upon the relation between the light energy incident in exposure and the change produced in development, the effect has been measured in terms of the optical density, determined by the capacity of the silver deposit to absorb light. It would be more logical if the effect of exposure were measured in terms of the quantity of metallic silver produced; and it is unfortunate that the measurement of the mass of silver in an image is so difficult, since it is probable that variation in the covering power of the silver plays a much larger part in photographic effects than is generally realized.

Hurter and Driffield[33] determined the relation between the density of a photographic image and the mass of silver per unit area. This ratio has been termed the *Photometric Constant*, but a better name would be *Photometric Equivalent.* They measured the density at a number of points and then determined the amount of silver in the image gravimetrically as silver chloride. They found that the density of plates developed in ferrous oxalate was directly proportional to the mass of silver and that a density of 1.0 corresponded to 0.0121 gram per square decimeter. In an independent measurement at a later date, for plates developed in pyrogallol they obtained essentially the same result and a lower value, 0.0104. Eder[34] confirmed the proportionality, finding the value 0.0103 for ferrous oxalate; and Sheppard and Mees, using both gravimetric and volumetric methods, found the same value as Eder.

Nutting[35] worked out a theoretical expression for the photometric equivalent for an emulsion made up of *m* layers of grains of single-grain thickness. In a layer one grain deep and one square centimeter in area, the projective area of all the blackened grains may be represented by A_1. Then A_1 and $(1 - A_1)$ are probabilities of stoppage and passage of a light ray. The probability of passing through m layers is $(1 - A_1)(1 - A_2) \cdots (1 - A_m) = T_m$, or the transparency. If all m layers average alike in grains, $A_1 = A_2$, etc., and $T = (1 - A)^m$. This corresponds to Beer's law in ordinary optical theory. Photographic density is related to transmission by the equation

$$D = -\log_{10} T = -\frac{1}{2.3}\log_e T. \qquad (53)$$

Thus,

$$D = -\frac{1}{2.3}\log_e (1 - A)^m. \qquad (54)$$

If A is small, then $D = mA/2.3$. But $A = na$ where a is the average area of a grain and n is the average number of grains per square centimeter in a layer one grain deep. Hence, $D = mna/2.3$. But the mass of silver is the number of grains times mean volume times "effective" specific gravity,* or $M = mnv\rho$. By division, the photometric equivalent, P, is found to be

$$P = 2.3\frac{v\rho}{a}. \qquad (55)$$

For spherical grains, the ratio of volume to projective area is $2/3\,d$, where d is the average diameter of the grains. Thus, the photometric equivalent for spherical grains is $1.53\,d\cdot\rho$. Experimentally, P is of the order of 10 mg. of silver per square decimeter of film, per unit density. Using this value of P and a size of grain 0.0001 centimeter in diameter, the value of ρ comes out 0.66 gm./cm.^{3}. This low value shows that the grain cannot consist of compact silver and accords well with the structure revealed by the electron microscope (Chapter VIII, p. 312, Figure 97).

Higson[36] worked out a theoretical expression for the photometric equivalent using a somewhat different approach. He considered the general case where light of intensity I falls on a colorless slab containing N black grains per square centimeter, the projective area of each grain being a square centimeters. The fraction of the area not covered by grains is T and the light transmitted is IT. If dN extra grains, of area adN, are added at random, they will cover the covered and uncovered portions of the slab in proportion to the areas of the covered and uncovered parts, *i.e.*, in the proportion $(1 - T) : T$. Accordingly, the area $a \cdot dN \cdot T$ of the part previously uncovered becomes covered, and the proportion $a \cdot dN \cdot TI$ of the light is cut off. The addition of dN grains changes the transparency by an amount $a \cdot dN \cdot T$; or

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* This term is used instead of the correct term, "density," because of the use of the latter for the photographic density, D.

$$-dT = adN \times T. \tag{56}$$

Therefore,

$$-\frac{dT}{T} = adN, \tag{57}$$

or

$$-\int_1^T \frac{dT}{T} = a\int_0^N dN. \tag{58}$$

Since $T = 1$ when $N = 0$,

$$D = -\log_{10} T = \frac{Na}{2.3}. \tag{59}$$

The mass of all the grains, N, per square centimeter is given by $M = Nv\rho$, where v and ρ are mean volume and "effective" specific gravity of the grains. Thus, the photometric equivalent, P, is found to be

$$P = \frac{M}{D} = 2.3\frac{v\rho}{a}, \tag{60}$$

in agreement with the formula derived by Nutting.

Arens, Eggert, and Heisenberg[37] give a theoretical treatment of the photometric constant in which they consider the importance of the shape factor of the grains. Their formula for density is

$$D = \frac{mna}{2.3} = \frac{Na}{2.3}, \tag{61}$$

this is the formula used by Nutting and Higson. If the area,

a, of a grain be expressed in terms of its mass, μ, and effective specific gravity, ρ, the formula is

$$D = \frac{N}{2.3} \cdot f \cdot \left(\frac{\mu}{\rho}\right)^{2/3}. \tag{62}$$

The factor f is a numerical constant depending upon the shape of grains in the emulsion. For cubic particles, $f = 1.0$; for spherical particles, $f = 1.21$; while for square plates whose thickness is 1/8 the length of a side, $f = 4.0$. From the relations $M = n\mu$ and $\delta = 1/P = D/M$, the equation is

$$\delta = \frac{f}{2.3} \mu^{-1/3} \rho^{-2/3}. \tag{63}$$

δ is the covering power and is equal to the reciprocal of the photometric equivalent P.

Arens, Eggert, and Heisenberg tested this equation for emulsions in which f and ρ were constant and the mass of grains μ was variable. Using several different types of development, they found that the variation with the grain mass μ was very closely in accord with the above equation. Using experimental values of δ and μ, they calculated the $(f/\rho^{2/3})$ values for a variety of development conditions and found this factor to vary from 10.3×10^{-4} to 5.4×10^{-4}. In the equation

$$P = 2.3 \frac{v\rho}{a}, \tag{64}$$

the value a must be considered the projected area of the grains supposed to be of uniform size. In fact, however, the sizes of developed grains in a film layer vary over a wide range determined by the distribution of size of the silver halide grains.

The question is whether one is justified in applying the equation given above using a as the average area of grains of a range of sizes. This question has been studied by Silberstein,* who finds that whatever the shape of the grains, the use of a range of grain sizes, instead of uniform grains, introduces only a numerical factor into the equation. In the case of spherical grains and an exponential distribution of grain sizes, such as may reasonably be expected, the factor is 1.33; *i.e.*,

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* Private communication.

$$P = 3.06 \frac{vp}{\bar{a}}, \tag{65}$$

where $\bar{a}$ is the average grain area.

It is seen that the optical density is not proportional simply to the mass of silver per unit area. Since the photometric equivalent is proportional to the diameter of the silver grains, it is unlikely to be independent of the exposure or the development of the material.

Meidinger[38] found that the equivalent is independent of exposure but that for emulsions of different grain size, its value decreases with decreasing size of grain.

Sheppard and Ballard[39] undertook an extensive study of the subject, using a method of analysis which enabled them to measure the mass of silver on photographic areas of only one square centimeter. They converted the silver to colloidal silver sulfide and compared the color of the solution with that of a standard in a micro-colorimeter. By the use of an instrument employing 2 cc. of solution, it was possible to determine two micrograms of silver with a fair degree of accuracy. Sensitometric strips were made on film, and small disks were punched out with a hollow steel punch. Then the gelatin was treated with strong sulfuric acid, and the silver was brominated with bromine water. Aqueous ammonia was added to dissolve the silver bromide, and then sodium sulfide solution was added. In a direct comparison of the micro-colorimetric method with gravimetric determinations on large areas, the agreement was

TABLE XII

Process Film		*Commercial Film*		*Eastman 33 Plate*	
D	*P*	*D*	*P*	*D*	*P*
0.21	0.0218	0.15	0.0214	0.44	0.0194
.35	.0214	.25	.0215	.53	.0197
.53	.0221	.41	.0203	.96	.0192
.89	.0167	.59	.0209	1.08	.0188
1.13	.0155	.85	.0188	1.90	.0196
1.34	.0147	1.19	.0176	2.00	.0179
1.58	.0134	1.55	.0166	2.75	.0164
1.87	.0123	2.32	.0149	4.47	.0149
2.07	.0113			4.64	.0140

excellent. Determinations could be made down to one microgram of silver, but on such a small amount the error was ±10 per cent. The results obtained showed that the photometric equivalent varies with the exposure and the development. Examples taken from their paper are given in Table XII.

The fact that the covering power of developed silver can vary enormously is shown by the figures determined for the silver equivalent of fog produced by extended development.

TABLE XIII

Time of Development	*Density*	*Gms. Silver per 100 cm.²*	*P*
32 mins.	0.35	0.010	0.029
64 "	.78	.025	.032
128 "	1.24	.058	.047
256 "	1.34	.066	.049
1024 "	1.34	.078	.058
	Original emulsion	0.083	

It is seen that nearly the whole of the silver was finally reduced, but with a final density of only 1.34. Yet, by sufficient exposure to light, this same amount of silver produced a density approaching, or greater than, 6.00. This difference cannot be due entirely to the "selective effect" by which fog starts more readily in the larger grains; it must also be connected with the influence of the rate of reduction of the grain, according to which, the slower the reduction, the more compactly the silver is deposited.

TABLE XIV

Log E	*Density*	*Gms. Silver per 100 cm.²*	*P*
No exposure	2.10	0.0503	0.0240
1.5	1.52	.0501	.0330
2.4	2.48	.0499	.0201
4.0	3.93	.0510	.0130

Another example of the astonishing variation of the photometric equivalent in the case of long-continued development leading to the production of fog is cited by Pritchard.[40] Motion-picture positive film exposed to X rays was developed for 2¾ hours and was then analyzed for silver content, with the results shown in Table XIV. It is seen that all the exposures gave the *same* amount of silver and that the variation in density is due solely to the variation in covering power of the deposit. It is probable that an explanation of these results could be found from a study of the structure of the deposit by means of the electron microscope.

Eggert and Küster[41] measured the relation between the diameter of the grains and the photometric equivalent of various emulsions under a variety of development conditions and found that the equation

$$P = 1.53 d\rho \qquad (66)$$

derived by Nutting for spherical grains holds very accurately. Their results are shown in Figure 72. The direct dependence of P upon grain diameter makes possible the expression of the photometric equivalent in terms of the Callier quotient Q. Callier[42] showed that the ratio Q of specular to diffuse density, $D''/D^{\ddagger}$, is closely related to grain size and increases with it. Measurements by Eggert and Küster[41,43] show that the relation is

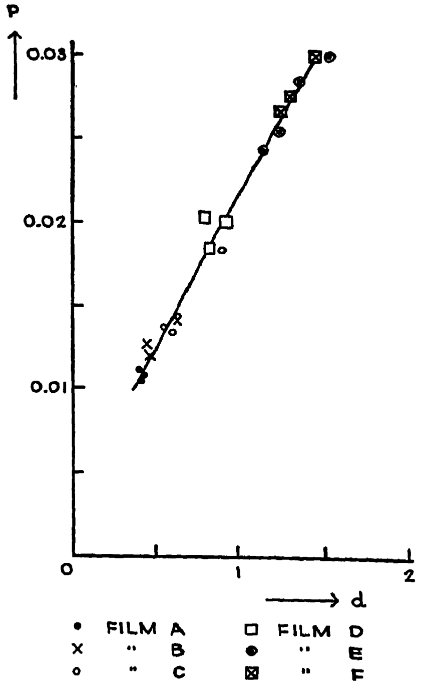

FIG. 72. The relation between the photometric equivalent and the diameter of the silver grains.

$$d = 6.8 \log Q. \qquad (67)$$

Using this value of d in equation 66,

$$P = 10.4\, \rho \log Q,$$

which is the relationship between P and Q. The nature of the Callier quotient and its relation to the printing density are discussed in Chapter XVII, p. 642.

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CHAPTER VI

THE RECIPROCITY, INTERMITTENCY, AND CLAYDEN EFFECTS

THE RECIPROCITY LAW FAILURE

In 1876, Bunsen and Roscoe[1] laid down a general law for photochemical reactions which states that the product of a photochemical reaction is dependent simply on the total energy employed, that is, on the product of intensity and time, and is independent of the two factors separately. From the reciprocal relation between time and intensity in the Bunsen-Roscoe expression, it was called the *reciprocity law*, and deviation from it is known as *failure of the reciprocity law.*

Scheiner[2] found in connection with the photographic photometry of stars that this relation was not strictly valid for the photographic emulsion. He noted that a change of 2.5 times in intensity in stellar photography, which corresponds to a change of one magnitude in star brightness, gave a change of only about 0.7 magnitude photographically. This work, therefore, caused the validity of the reciprocity law to be questioned.

In 1893, Abney[3] verified Scheiner's results by sensitometric measurements. Working with two different light sources, a candle and an electric spark, he obtained evidence that the efficiency of the photographic process was a maximum at one intensity level and that the efficiency decreased at extremely high and low intensities. Abney thus demonstrated that there is one intensity level at which the photographic effect proceeds most efficiently.

Schwarzschild[4] (1899) confirmed Abney's results that the reciprocity law is not valid and concluded that a constant effect is produced as long as the condition

$$It^p = \text{constant} \tag{1}$$

is satisfied, in which p is constant and equal to about 0.8. This relation, with p constant, came to be generally known as *Schwarzschild's law* and is frequently referred to by this name today.

However, it is now well known that this relation, with p constant, is not a valid criterion for determining a constant photographic effect over very wide ranges of intensity. The reason Schwarzschild obtained his result is that he was an astronomer working in the region of extremely low intensities with exposures varying from a few minutes to several hours, and the above expression with p constant could be applied with considerable accuracy over the limited range in which he was interested.

In 1901, Englisch [5] made measurements of the reciprocity law failure which agreed with Abney's work and found that the exponent p is variable.

Sheppard and Mees [6] (1903–1906) found that there is an intensity at which the photographic effect is a maximum for a given exposure. In their work, the measurements were extended to a wider range of intensities than those used previously. They established the fact that, if an equation of the type

$$It^p = \text{constant} \tag{2}$$

is to be used to express the exposure condition required to give constant density, p must be a variable changing from a value of less than unity at low intensities to a value greater than unity at high intensities.

The true form of the relation between intensity and the effectiveness of exposure was first given by Kron,[7] who in 1913 carried out an extensive investigation of the reciprocity law failure.

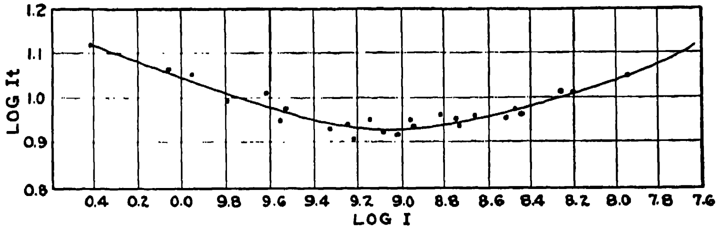

FIG. 73. Reciprocity failure curve for constant density (Kron).

Kron gave his results in the form of constant density curves; that is, he plotted against the logarithm of intensity the logarithm of exposure (It) required to produce a constant density. One of Kron's curves is shown in Figure 73. For all the emulsions studied, he found an optimal intensity, or an intensity at which a minimum amount of exposure is required to produce a given density. Kron attempted to formulate a general law by which he could represent the reciprocity law failure for any emulsion and found that his curves of constant density were well represented by the hyperbolic equation

$$\log It = \text{constant} + a\sqrt{(\log I/I_0)^2 + 1}, \tag{3}$$

in which a and I_0 are constants varying with different emulsions. The constant a governs the shape of the curves and is thereby a measure of the extent of the reciprocity law failure, while I_0 corresponds to the optimal intensity. Kron's measurements were applied extensively by Halm [8] to the photographic photometry of stars. In this work, Halm preferred to use the catenary equation

$$\log It = \text{constant} + \log [(I/I_0)^a + (I/I_0)^{-a}], \tag{4}$$

which was an alternative equation originally suggested by Kron to represent the reciprocity failure curves. Halm found that this equation gave as good agreement with the experimental curves as the hyperbolic equation, and he considered it more desirable for practical use because it reduces at extremely low intensity to the simplified equation

$$\log It = \text{constant} - a \log I, \tag{5}$$

which in its linear form becomes

$$It^{\frac{1}{1 \pm a}} = \text{constant}, \tag{6}$$

which is the Schwarzschild equation when $p = 1/(1 \pm a)$. Curves representing the various equations for constant density are shown in Figure 74. Curve A is the catenary; curve B, the hyperbola; and the straight sloping lines CC' represent the Schwarzschild equation, It^p = constant. The horizontal straight lines, DD', represent the Bunsen-Roscoe reciprocity law in the region near optimal intensity, where deviations from the law are less than 5 per cent.

Helmick [9] (1918–1921) carried on studies of the reciprocity law failure, using monochromatic light of different wave lengths.

In agreement with previous workers, he found a very definite optimal intensity for all emulsions tested by him.

During the period 1923 to 1927, an extended investigation was made by Jones[10] and his co-workers. They carried out measurements on various types of emulsions over wide ranges

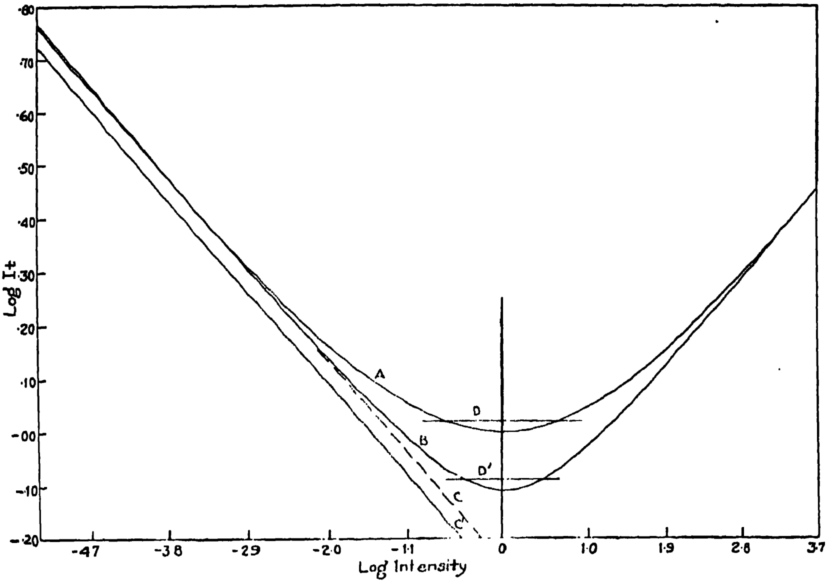

FIG. 74. Curves corresponding to various suggested equations for reciprocity failure: A, catenary; B, hyperbola (Kron); C, C′ (Schwarzschild); D, D′, Bunsen-Roscoe law.

of intensity and studied the effect of development upon the reciprocity law failure. Particular attention was paid to finding the correct relationship between the intensity and time factors of exposure. In agreement with Halm, they found that the catenary equation fitted their experimental results better than any other type that had been suggested. A typical family of reciprocity failure curves obtained by these workers is shown in Figure 75.

In 1927, Arens and Eggert[11] published their experimental results on reciprocity law failure. They advocated a new method of presenting results on the subject. Instead of plotting values of log *It* *vs.* log *I* for constant density, the authors plotted log *I* as a function of log *t* for constant densities. By variation of the density, a family of curves is obtained between the variables $\log I$ and $\log t$ (Figure 76). The slope of these curves at any point represents the value of the Schwarzschild coefficient p and, therefore, is a measure of the reciprocity law failure. If there is no reciprocity law failure, the $\log I$, $\log t$ curves are straight lines of slope -1. One of the chief points in favor of the system of Arens and Eggert is that symmetrical roles are given the variables $\log I$ and $\log t$.

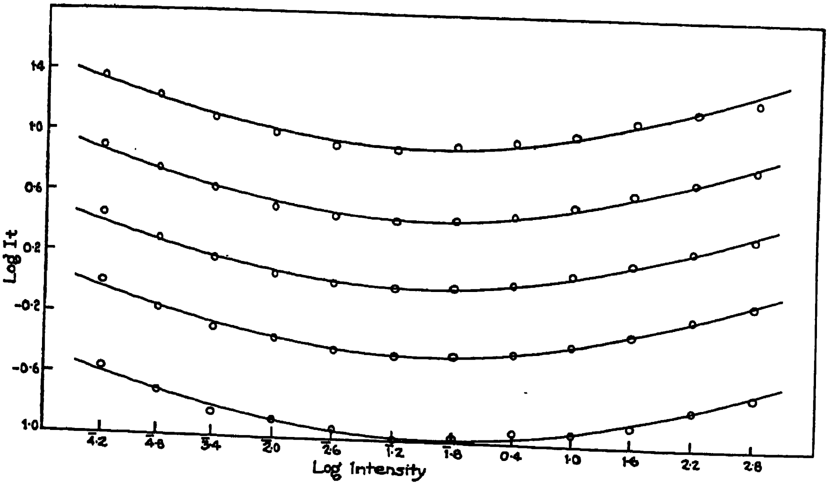

FIG. 75. Reciprocity failure curves for constant densities: ○, experimental values; solid lines calculated from catenary equation.

The method of representing reciprocity law failure outlined above is actually but a part of a more general system put forward by Arens and Eggert for representing sensitometric data. According to this general system, the variables D, $\log I$, and $\log t$ play equally important roles. By using, in turn, D, $\log I$, and $\log t$ as the variable parameter, three families of curves can be obtained, as follows:

Independent Variable	*Dependent Variable*	*Parameter*	*Name of Curve*
$\log t$	D	$\log I$	Time Scale
$\log I$	D	$\log t$	Intensity Scale
$\log t$	$\log I$	D	Constant Density

The gradients of these three families of curves may be denoted by $g(t)$, $g(I)$, and $-p$, respectively.

The difference between time scale and intensity scale characteristic curves is due to the failure of the reciprocity law. If this law were valid, both scales would be identical. This raises

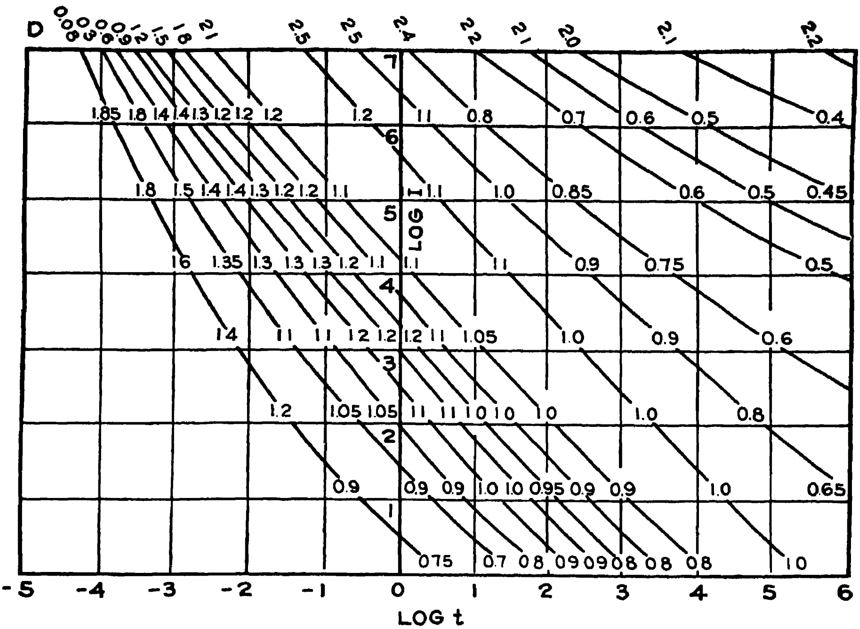

FIG. 76. A plot of p values on the log I, log t plane for different density values.

the question of the connection between the three gradients $g(t)$, $g(I)$, and p. Since p is the gradient for a curve, D = constant,

$$dD = 0 = \frac{\partial D}{\partial(\log I)}\, d(\log I) + \frac{\partial D}{\partial(\log t)}\, d(\log t), \tag{7}$$

or

$$-\frac{d(\log I)}{d(\log t)} = p = \frac{\partial D/\partial \log t}{\partial D/\partial \log I} = \frac{g(t)}{g(I)}. \tag{8}$$

This formula is discussed also by Ross,[12] de Langhe,[13] and Narath.[14] For those portions of the $(D, \log t)$ and $(D, \log I)$ curves for which $g(t)$ and $g(I)$ are equal to γ_t and γ_I, respectively, the Schwarzschild coefficient p is given by

$$p = -\frac{\gamma_t}{\gamma_I}. \tag{9}$$

In relation to the reciprocity law failure, there are three characteristic regions of intensity corresponding to the three conditions:

$p < 1,$	$\gamma_t < \gamma_I$	low intensity
$p = 1,$	$\gamma_t = \gamma_I$	optimal intensity
$p > 1,$	$\gamma_t > \gamma_I$	high intensity

This is a very useful scheme for relating the Schwarzschild coefficient and the γ values of the intensity and time scale curves to the different regions of intensity.

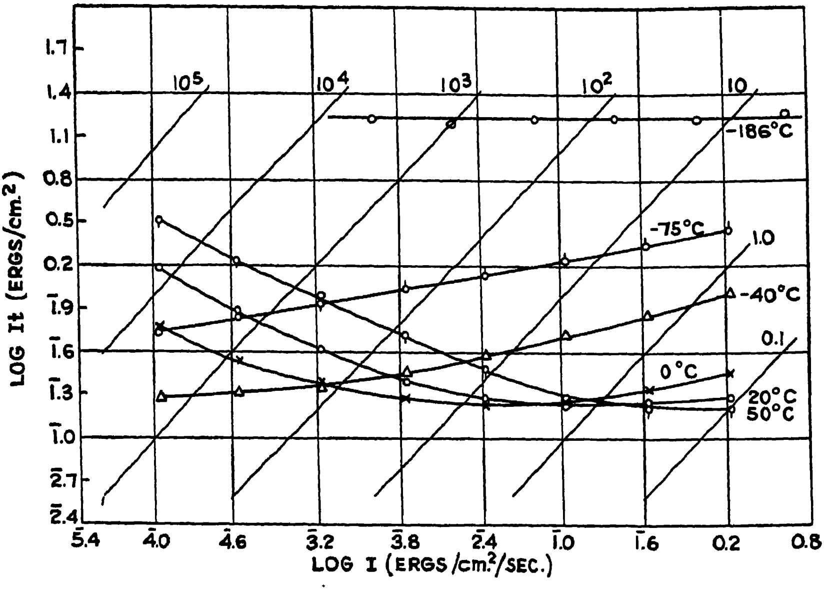

FIG. 77. Curves showing variation of reciprocity law failure with temperature.

From the measurements that have been made on reciprocity law failure, it can be said generally that the reciprocity characteristic varies greatly with different emulsions. However, there appear to be no general rules by which the reciprocity law failure can be related to other attributes of the emulsion, such as speed, grain size, or color sensitivity. The curves are usually symmetrical for a considerable range about their minimum point but frequently turn sharply upward at low intensities. The exposure intensity at which maximum efficiency occurs is about that value for which a medium density is produced in from 0.1 to 10 seconds. The shape of the curve varies little with the time of development except for slight shifts in optimal intensity.

It has been found [15] that the reciprocity law failure displays a marked variation with temperature. A series of reciprocity failure curves for temperatures from 50° C. to −186° C. is shown in Figure 77. It is seen that with a decrease of temperature, the high-intensity end of the curve rises continually, while the low-intensity end of the curve at first falls and then moves upward. At a sufficiently low temperature, the reciprocity law failure disappears, as shown by the curve for −186° C.

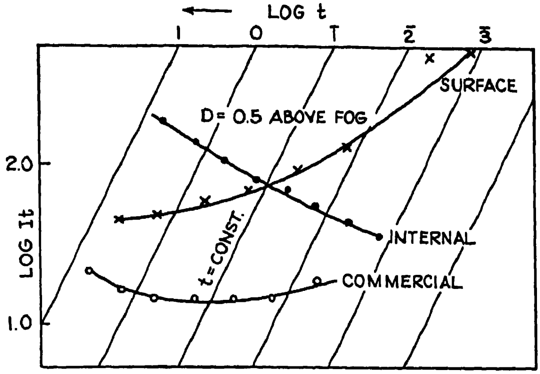

FIG. 78. Reciprocity curves with surface, internal, and commercial developers.

This behavior of the reciprocity characteristic with temperature suggests that the reciprocity failure curve results from the superposition of two separate and distinct phenomena, one of which predominates at high intensity and the other at low. A similar conclusion may be drawn from the study by Berg, Marriage, and Stevens [16] of the reciprocity failure shown by materials developed for the surface and internal latent images, respectively (Chapter IV, p. 169). Three of their reciprocity curves are shown in Figure 78—one for a strip developed in an ordinary commercial developer; the second, in a special developer adapted to develop the surface latent image; and the third, in a developer containing a silver solvent which removes the surface and utilizes the interior nuclei. It is seen that the curve for the internal image slopes in a direction opposite that of the curve for the surface image, which suggests that with low intensities, the surface nuclei are favored at the expense of the interior nuclei. In these experiments, the internal latent image did not tend to decrease with increasing intensity even at the highest intensities used.

The High-Intensity Effect

On the basis of the theory of latent-image formation proposed by Gurney and Mott, the reciprocity law failure at high intensity is attributed to the sluggishness of the secondary process of latent-image formation, which consists of the migration of silver ions to the speck. For exposures at high intensity, the migration of silver ions cannot occur as rapidly as the primary, electronic part of the latent-image process. This prevents immediate neutralization of the electronic charges as they are trapped at the sensitivity specks. The negative charge on the specks repels further electrons and thereby limits the subsequent rate of trapping of electrons to that at which silver ions can reach the speck. The first thought is that these electrons recombine with bromine atoms, but the experiments of Berg, Marriage, and Stevens[16] referred to above furnish evidence that the majority of the electrons contribute to the formation of latent-image nuclei in the interior of the grain, where they are unavailable for development. This is in accord with the theory proposed earlier by Lüppo-Cramer[17] that the reciprocity law failure at high intensity results from the formation of increasing amounts of internal nuclei with increasing intensity. The shift upward of the high-intensity end of the reciprocity failure curve with lowered temperature can be explained in the same way. As the temperature is lowered, the mobility of the silver ions is reduced, since the rate at which they can migrate to the specks is decreased. Therefore, in the region of high intensity, where exposure times are short and ionic mobility becomes an important factor in emulsion sensitivity, reduction of temperature results in a lowered emulsion sensitivity. In this region, a decrease in temperature has the same effect as an increase of light intensity, since either effectively slows up the ionic mobility relative to the rate of charging the speck. This is shown in Figure 77.

Finally, if the temperature is lowered sufficiently, the reciprocity law failure disappears. The curve for −186° C. is horizontal, showing no effect of the intensity level upon exposure. At this temperature ionic mobility in silver bromide is so low that no appreciable movement of silver ions can take place during an ordinary exposure. Experimental evidence for this is given in Figure 79, showing interrupted exposures at low temperature. It may be supposed that at −186° C. the electronic process of latent-image formation alone takes place during the exposure period and that the secondary ionic process occurs only after the emulsion is warmed up for development. Under these conditions, there should be no effect of the intensity level since, in the absence of any neutralizing effect of the ions, the rate of charging the speck would be immaterial.

On the basis of this discussion, it is readily seen that, for any temperature, the influence of intensity level upon the photographic effect should disappear, provided that the exposure period is sufficiently short. This is because, for extremely short times, the exposure to light and, therefore, the electronic part of the latent-image process would be completed before the silver ions could move appreciably. The exposure time required to bring about this condition would become shorter with rising temperature. At liquid-air temperature, the condition is seen to hold for all exposure times covered in Figure 79. Berg [18] investigated this problem at room temperature and found that the reciprocity failure curves do flatten out at extremely short exposure times. According to Berg's results, the bend-over point occurs in the neighborhood of 10^{-6} seconds.

Low-Intensity Effect

The failure of the reciprocity law at low intensity corresponds to a drop in the efficiency of the photographic process with lowered intensity. In Figure 77, it is seen that this effect is diminished by a decrease in temperature. This experimental fact has led to the suggestion [19] that the low-intensity reciprocity law failure arises from a regression of the latent image by thermal motion. To account for the effect of lowered intensity, it is necessary to assume that this regression takes place more readily in the initial stages of formation of the speck than in the later

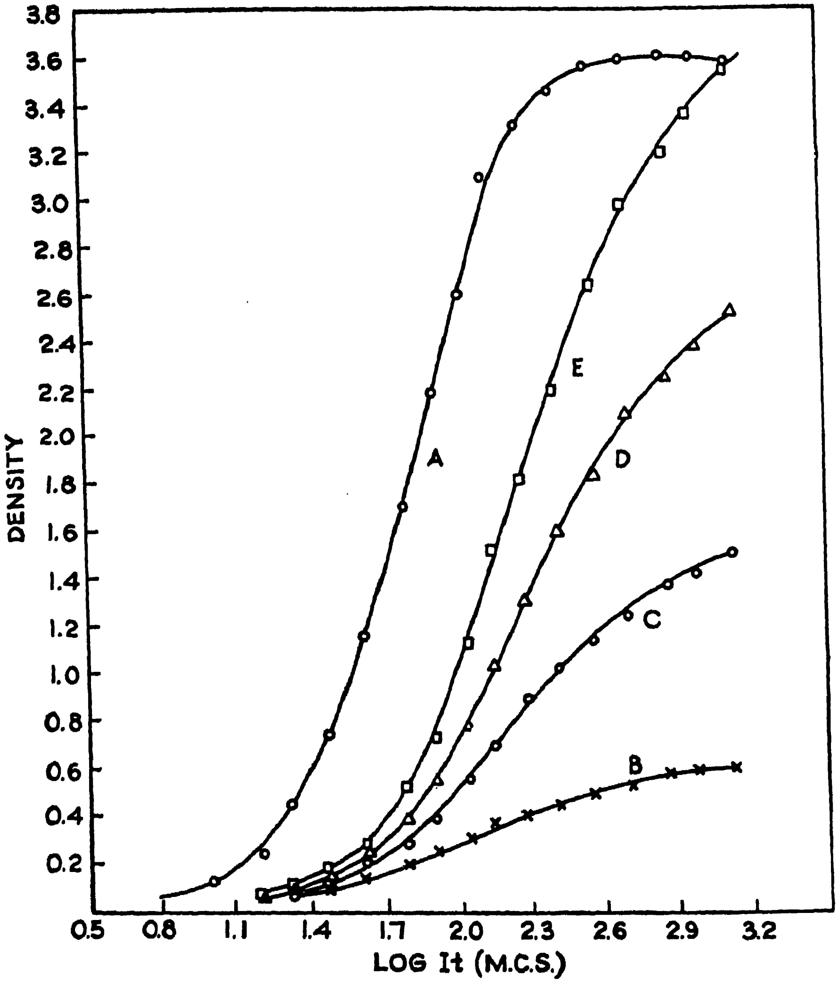

FIG. 79. Characteristic curves showing the effect of interrupted exposures at low temperatures:

Curve	*Expos. Temp.*	*Expos. Time*
A	20° C.	1–160 sec. flash
B	−186° C.	1–160 " "
C	−186° C.	2– 80 " "
D	−186° C.	4– 40 " "
E	−186° C.	8– 20 " "

B, *C*, *D*, *E* emulsions warmed to 20° C. after each flash.

stages. Thus, for a low-intensity exposure, when the speck forms slowly and exists for some time as a clump of only a few silver atoms, the speck would be more likely to be broken up. The disintegration of the speck is supposed to proceed by ejection of an electron from the speck into the surrounding silver bromide grain, followed by the diffusion away of a silver ion. If the regression is considered to be due to the thermal ejection of electrons, the observed suppression of this effect with lowered temperature is to be expected.* If the temperature is lowered sufficiently to eradicate this regression action, further decrease in temperature results in a decrease of sensitivity in accord with the lowered ionic mobility, as described previously. When this stage is reached, there remains only the high-intensity component of reciprocity law failure, which then manifests itself even for long exposure times.

That the low-intensity component of reciprocity law failure results from disintegration of the latent-image speck in its initial stages of formation has received some support in experiments carried out by Weinland[20] and Webb and Evans.[21] The following is a description of one of the experiments by Webb and Evans:

An emulsion was given a series of equal energy exposures, each exposure consisting partly of high-intensity, H.I., and partly of low-intensity, L.I., light. The intensity level of the H.I. part was nearly optimal, while that of the L.I. part was lower by a factor of one thousand. The results of a series of such exposures, in which the relative proportions of H.I. to L.I. were varied through the range of zero to one, are shown in Figure 80. The upper curve of the loop corresponds to the condition that the H.I. part of the exposure was made first and the L.I. part second, while the lower curve corresponds to the reverse condition. For both curves, the relative proportions of H.I. to L.I. exposure were varied through the steps indicated by the diagram at the bottom of the figure. The reciprocity law failure for the emulsion between the intensity levels H.I. and L.I. is shown by the difference in density between the extreme left point (all high-intensity exposure) and the extreme right point (all low-intensity exposure). The difference in shape of the two curves between these two points is attributable to the difference in the time order of the exposures. It is seen that if the H.I. part of the exposure is applied first, the L.I. part of the exposure is always rendered more efficient. In fact, for the case illustrated, if the H.I. exposure is given first and amounts to as much as one-fourth the total exposure, the L.I. part of the exposure is rendered just as efficient as if the exposure were made entirely at high intensity. On the other hand, if the order of the exposures is reversed, the L.I. part being applied first, the drop in efficiency of the L.I. exposure is very marked. The interpretation that has been given these results is that the reciprocity law failure at low intensity takes place principally in the initial stages of exposure while the speck is still small. If a sufficient amount of

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* While the origin of the regression in spontaneous thermal decomposition agrees with the suppression of the effect by lowered temperature, that fact does not necessarily indicate a thermal origin of the regression. If the regression of the image were due to chemically induced action, it would also disappear at low temperatures. The possibility of a chemical action leading to regression is suggested by the variation of the reciprocity failure with the procedure followed in making the emulsion.

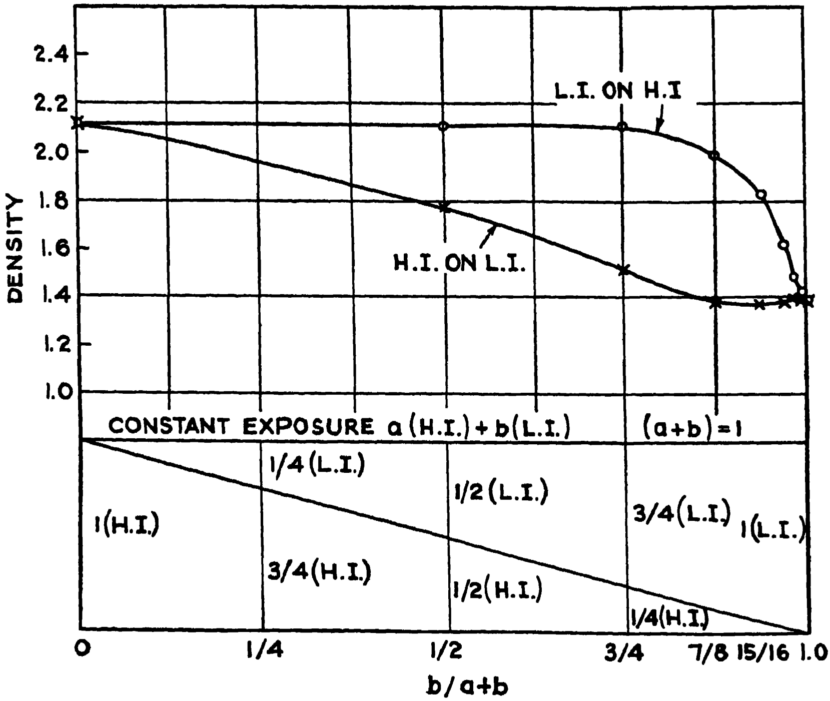

FIG. 80. Curves showing the effect of equal energy, mixed exposures, partly at high intensity and partly at low intensity.

exposure is given first at high intensity, a stable speck is established, which can be completed with low-intensity light. This experiment also demonstrates the important fact that a stable latent-image speck can exist which is not yet developable. This is supported by the work of Brentano and Baxter,[22] who found that for intermittent exposures below the threshold the effect is simply the sum of the single exposures.

Effect of Wave Length upon Reciprocity Law Failure

An important characteristic of the reciprocity law failure is its relation to the wave length of the exposing radiation. If the reciprocity failure curves for a given material and development condition are plotted so that the abscissa is the logarithm of the time factor of exposure, the curves for different wave lengths have the same shapes but are displaced vertically from one another [23] (Figure 81). The shapes of the curves depend upon density and time of exposure, whereas their heights depend upon density and wave length. This effect can be expressed in analytical form by the functional equation

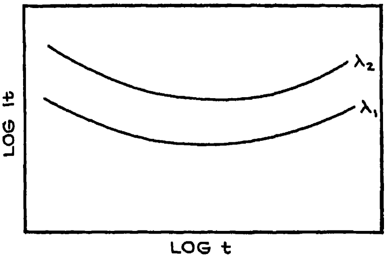

Fig. 81. Reciprocity failure curves for light of different wave lengths.

$$\log It = F_1(D, t) + F_2(D, \lambda). \tag{10}$$

By rearranging the terms of this equation and using antilogarithms, the equation

$$S(D, \lambda)It = X(D, t) \tag{11}$$

is obtained, where $S(D, \lambda)$ represents the spectral sensitivity of the emulsion in reciprocal energy units required to produce a given density D. According to equation (11), the spectral sensitivity of an emulsion is independent of exposure time in the sense that the relative *amounts* of exposure required to produce the same density at two wave lengths remain constant for any *time* of exposure provided that the exposure *times* for the two wave lengths are the same. This result is closely related to the law discovered by van Kreveld (Chapter XVIII, p. 687), according to which the photographic emulsion behaves additively for radiation of different wave lengths. (See also Chapter V, p. 224.)

The above results can be explained qualitatively by the Gurney-Mott theory, according to which the sensitivity of an emulsion to different wave lengths depends upon the degree to which different wave-length radiations can produce photoconducting electrons. After an electron is in the conduction band, it is like any other electron in the conduction band, and whether it was placed there by a blue or a red quantum of radiation is therefore immaterial. The efficiency with which the electrons are utilized in latent-image formation, which depends upon the rate at which they are raised into the conduction band, determines the magnitude of the reciprocity law failure. It is thus seen that the important factor for reciprocity law failure is the time rate of formation of the latent image. If exposures to different wave-length radiations are compared on the basis of equal densities in equal times, it is to be expected that the reciprocity failure curves would run parallel.

THE INTERMITTENCY EFFECT

An effect closely associated with the reciprocity law failure is the so-called *intermittency effect.* The density produced by an exposure given in a number of discrete installments is, in general, different from that produced by a continuous exposure of the same energy.

A quantitative study of the effect of intermittent exposures was first carried out by Abney [24] in 1893. In this work, the effects of light intensity, ratio of light to dark period, and speed of interruption of the exposure were investigated; and it was found that all of these factors influenced the results. Abney found that in all cases the intermittent exposure gave a smaller photographic effect than an equal-energy continuous exposure.

In 1899, Englisch [5b] made measurements from which he studied the behavior of the intermittency effect. In agreement with Abney, he found that the intermittent exposure was always less efficient and that it was dependent upon the intensity of light in the light period, the amount of light given in each flash, and the rate of interruption.

Schwarzschild (1899)[25] carried out further experiments on the intermittency effect, and from his results concluded likewise that the intermittent exposure always gives a smaller effect than the continuous exposure. He confirmed the results obtained earlier by Abney and Englisch with regard to the effect of the intensity of light and the ratio of light to dark period.

In an effort to determine the extent to which the results of practical sensitometric tests made with rapidly rotating sectors are affected by the intermittency effect, Sheppard and Mees (1903)[26] carried out tests on the intermittency effect. They found that, for sufficiently low frequency of flash, the results were very nearly the same as for an equal-energy continuous exposure.

In 1914, Weber[27] carried out experiments to test the validity of the use of intermittent exposures in spectrophotometry. He found that if the over-all exposure time is long and the exposure is broken into a sufficiently large number of interruptions, the effect of an intermittent exposure is equivalent to that of a continuous exposure of the same energy and remains so for all higher numbers of interruptions.

Howe[28] (1916), working with the Hilger sector photometer, came to the same conclusion as Weber; namely, that intermittent and continuous exposures of the same over-all time and energy produce equal photographic effects under the conditions of low intensity and large number of interruptions. Similar experiments carried out by Martin on the Hilger sector photometer[29] (1918) confirmed the findings of Howe and Weber.

In 1926, Baker[30] carried out an investigation on the intermittency effect and concluded that an expression similar to that proposed by Schwarzschild for continuous light could be used to express this effect; namely,

$$f(D) = It^{\pi} \tag{12}$$

where D = density
I = illumination
and t = duration of actual exposure to light.

If the sector is revolved only once, π will be equal to the Schwarzschild index p, but if the intermittent exposures integrate, π will become unity for sufficiently high sector speeds. Baker's research showed that the deviation of π from unity for speeds giving sixty flashes a second is less than one per cent.

Weinland[31] (1927) studied the intermittency effect with light of several wave lengths between 254 mμ and 436 mμ. His results indicated a close connection between the intermittency effect and the reciprocity law failure, although he worked at only low intensities; the intermittency effect always seemed to follow the reciprocity law failure but to be of smaller magnitude.

Davis[32] (1926–27) carried out an extensive series of measurements on the intermittency effect, using three different types of emulsions and a wide range of intensities. He obtained the important result that an intermittent exposure made at a sufficiently high intensity of illumination produces a greater effect than an equal-energy continuous exposure. This was the first time that this was reported. Davis studied the intermittency effect at all parts of the exposure curve and showed that it might be positive in the toe of the curve and negative in the shoulder, or vice versa.

During the period 1931–1933, O'Brien[33] and his co-workers carried out a series of measurements on the intermittency effect and the reciprocity law failure for photographic emulsions. These experiments were made with a great deal of care: The reciprocity failure was measured by comparing two intermittent exposures, A and B, of the same ratio of light to dark period but of unequal intensities in the flash periods. The intermittency effect was then measured by comparing two intermittent exposures, B and C, of equal intensity but of different ratio of light to dark period. The B exposures were thus common to both experiments. It was found that the reciprocity law failure and the intermittency effect exactly compensate each other, provided that the frequency of flash is above about ten flashes a second. Stated in another way, the reciprocity law failure and the intermittency effects, as measured in the above experiments, become equal in magnitude when viewed from the standpoint of average intensities.

Webb[34] (1933) undertook an investigation of the problem of the intermittency effect and its relationship to reciprocity law failure. From experiments carried out comparing continuous and intermittent exposures of the same average intensities, it was definitely shown that the intermittency effect is not a separate and independent phenomenon but is a manifestation of reciprocity law failure. The effect produced by an intermittent exposure always lies between those produced by two continuous exposures: one of intensity equal to that of the flash period and the other of intensity equal to the average intensity of the comparison intermittent exposure. Continuous and intermittent exposures of the same average intensity become equal in their effects when the frequency of flash of the intermittent exposure surpasses a certain critical value, which depends upon the intensity level.

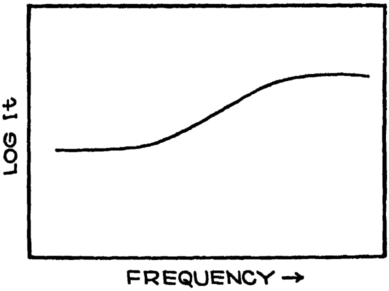

Fig. 82. Intermittency effect as a function of frequency of flash.

A typical curve showing the variation of the intermittency effect with varying frequency of flash is shown in Figure 82. This curve represents the amount of exposure required to produce constant density as a function of the frequency of interruption in flashes per second for the intermittent exposure. The curve rises or falls, depending upon whether the exposing intensity is above or below optimal intensity. The relatively flat part of the curve at low frequencies of flash is readily understood since breaking an exposure into a few installments would alter the exposure distribution only slightly from that in the original continuous exposure. Gradually, however, as the frequency is increased, the curve rises and approaches asymptotically the value, corresponding to the exposure value required for a continuous exposure, of intensity equal to that of the average intensity of the intermittent exposure. The equivalence of continuous and intermittent exposures at high frequency of flash is attributed to the reproduction in the intermittent exposure of the haphazard nature of the exposure of a single grain in the continuous exposure. It may be realized that an abnormally high frequency of flash is not essential for this purpose if it is considered that the rate of incidence of quanta on a single photographic grain is rather moderate even in a relatively high intensity exposure. Theoretical investigation[35] shows that the condition of equivalence of the two types of exposure results if the frequency of flash of the intermittent exposure is approximately equal to the average rate of incidence of quanta on the sensitive area of the photographic grain.

Accepting this as a criterion of lack of distinction between a continuous and intermittent exposure, a value for the sensitive area of the photographic grain can be found from experimental determinations of the critical frequency; this value is of the order of the area of the grain itself.

THE CLAYDEN EFFECT

Another effect which should be considered before leaving this subject is the so-called *Clayden effect.* If a photographic emulsion is given a very brief exposure to light of extremely high intensity and a subsequent exposure to light of moderate intensity, the two exposures do not add in a simple manner. This effect was discovered by Clayden[36] in 1899 in connection with photographic exposures to lightning flashes. The very high intensity short-time exposures of the images of the lightning streaks were overlaid by a general exposure of much weaker intensity, and the images of the lightning discharges appeared reversed compared with the surrounding density. This effect, which has been observed by many later workers, is often referred to by the name of "black lightning." The effect can be produced equally well by exposure to electric sparks.[36] It was thought by some of the early workers that it might be due to some peculiarity of the light of the electric discharge.

In 1903, Wood[37] demonstrated for the first time that the effect could be produced by any type of light source provided only that the intensity of the pre-exposure was sufficiently high and the duration of the exposure short enough. He found that 1/1000 second was about the longest time which would produce the effect and that it was much more pronounced for exposures of the order of 1/10,000 second. Wood further investigated the effect of other stimuli and found that if they are arranged in the order of pressure marks, X rays, light shock, and low-intensity light, an impression of any one of them can be made to appear reversed by subsequent exposure to any other in the list following it but, under no circumstances, by exposure to any one preceding it. For example, pressure marks can be reversed by any of the other three stimuli, while X-ray images are reversed only by light shock and low-intensity light.

The reversal effect obtained with X rays followed by light is known as the *Villard effect*, having been discovered by Villard [38] in 1900. This effect has received much attention from later experimenters [39] and is generally believed to be a special case of the Clayden effect. Further work on the Clayden effect using ordinary light exposures has been carried out by Landau.[40]

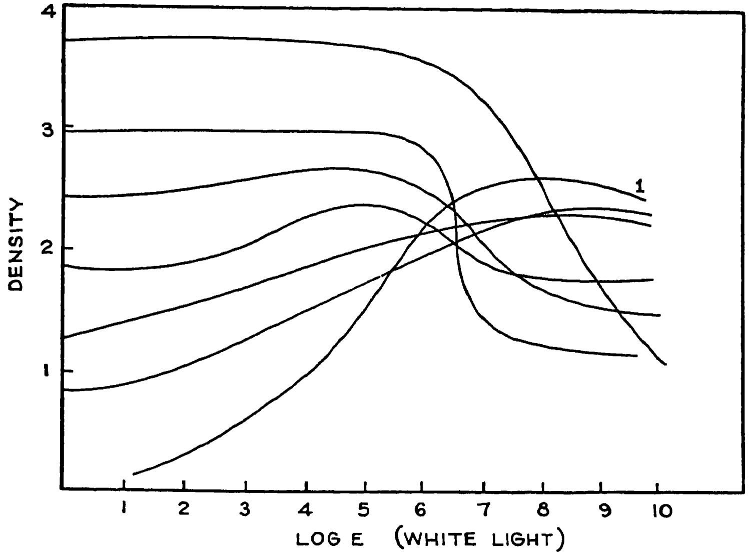

FIG. 83. Density-log exposure curves obtained by various amounts of pre-exposure to X rays with superposed time-scale exposures to white light.

The Clayden effect is not a reversal effect in the true sense of the word; at least, true reversal action does not necessarily accompany it. The feature which characterizes the Clayden effect is that the initial exposure to the high-intensity light desensitizes the emulsion, so that subsequent exposure to weak intensity light produces less effect than if the pre-exposure had not been given. It does not *require* that the effect produced by the original high-intensity exposure be reduced by the second exposure, although this may occur. As usually observed, the density resulting from the two superposed exposures is less than that of the single exposure to the low-intensity light, making it appear that the effect is a reversal.

According to the intensity used in the pre- and after-exposures, a variety of conditions can be set up with regard to the resulting density. This is well portrayed by the curves shown in Figure 83, which is taken from a paper by Volmer.[39c] Different portions of a photographic plate were given pre-exposures of varying amounts to X rays. Then a subsequent exposure was given to a time-scale variation of weak light. It is seen that the action of the after-exposure to weak light may enhance, leave unchanged, or diminish the action of the original exposure. The condition that the combined effect of both exposures is less than that of the after-exposure alone is the condition usually referred to as the Clayden effect. It may be seen from Figure 83 that this is only a special case of the general phenomena attending the addition of high- and low-intensity exposures.

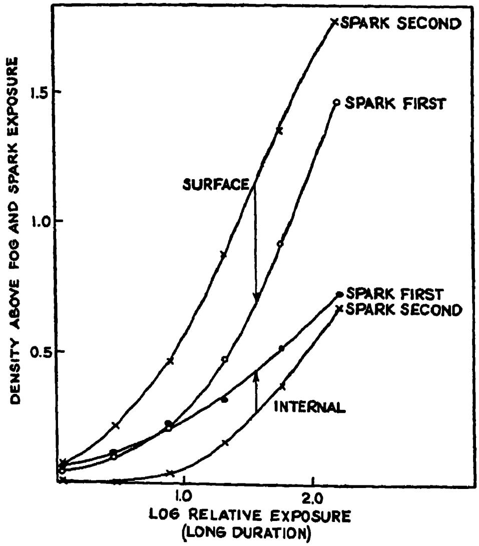

FIG. 84. Characteristic curves obtained from a uniform spark exposure given before and after a long-duration step-wedge exposure against which the density above fog and spark density is plotted, for internal and external development.

Various workers have attempted to give a theoretical explanation of the cause of the Clayden effect.[39c,41] One theory supposes that in the very high-intensity, short-time pre-exposure, the large number of silver atoms formed so suddenly in each photographic grain tend to form a large number of nuclei. It is then supposed that the action of the secondary exposure to low-intensity light coalesces these dispersed nuclei into larger nuclei, thus reducing the active surface of the silver nuclei for development. This coalescing action is supposed to occur by nuclei growing into each other or by the larger nuclei "absorbing" the smaller ones. No very clear explanation has ever been given of how this process could occur. Lüppo-Cramer [42] attributed the Clayden effect to the formation of internal latent images when the intensity of the light is very high. Kempf [43a] and Kornfeld [43b] showed that high-intensity exposures do produce internal nuclei, which can be developed in solutions containing solvents for silver bromide. In their study of the surface and internal latent images (Chapter IV, p. 169), Berg, Marriage, and Stevens [44] exposed photographic materials to a combination of high- and low-intensity light sources using the crossed wedge method. The high-intensity exposure was carried out by exploding a piece of fine tungsten wire by means of a condenser discharge, while the low-intensity exposure was for ten seconds' duration to a low-intensity lamp. The exposures were first applied in the order of high intensity followed by low intensity and then in the reverse order. Strips of film given these two types of exposure, respectively, were developed for the surface and internal latent images, with the results shown in Figure 84. A strong Clayden effect was obtained with surface development, as shown by the decreased density obtained if the high-intensity exposure preceded that of low intensity. On the other hand, the reverse effect was observed for the internal latent-image development. These results are readily understood if it is assumed that the high-intensity exposure, if given first, forms a large number of internal latent-image nuclei which act as traps for the product of the second exposure to weak light. The desensitization for the surface latent image corresponds to a complementary sensitization for the internal latent image.

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CHAPTER VII

SOLARIZATION AND THE HERSCHEL, SABATTIER, AND ALBERT EFFECTS

If areas of a photographic emulsion layer are exposed to increasing amounts of light, the densities produced after development will not increase indefinitely but will reach a limit and then, with continued exposure, will diminish somewhat. This is known as *reversal* or *solarization*.* Thus, after a certain degree of exposure has been reached, further exposure of the photographic grain tends to destroy the developable state induced by the earlier part of the exposure. Different emulsions exhibit this effect to varying extents, and only specially prepared emulsions show it strongly. Moreover, a clear reversal of the increase of density with exposure occurs only with limited development; if development is carried to completion, the reversal disappears.[1] Figure 85 shows the results obtained by Wilsey and Pritchard from exposures of portrait film to light. It is seen that the maximum reversal of the curve is obtained with moderate times of development (two or three minutes) and that reversal disappears after a development of sixteen minutes.

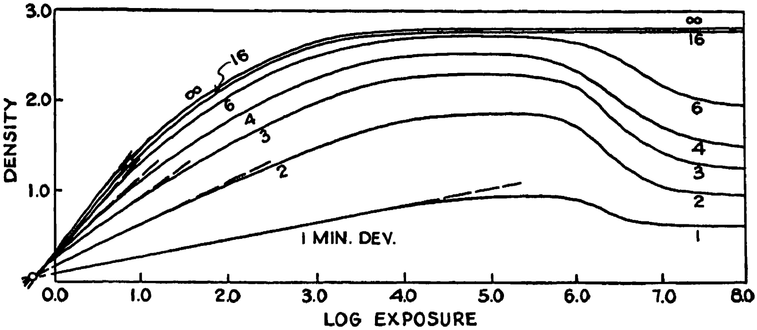

FIG. 85. The effect of development time on solarization (Wilsey and Pritchard).

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* The term *solarization* was originally given to highly over-exposed print-out images in which a change of reflectance of the image occurred, producing bronzed shadows.

The relation of solarization to the time of development was studied by Arens[2] in the course of his extensive investigations upon the phenomenon, and one of his typical results is shown in Figure 86. It is seen that with four minutes' development the curve shows typical solarization; after thirty minutes, the whole curve rises, and the most heavily exposed portion shows *re-reversal;* while after sixty minutes' development, solarization disappears. Arens demonstrated these effects of development very clearly by plotting the density against the logarithm of the time of development (Figure 87). The curves marked *n* are for densities resulting from exposures in the normal exposure region of the characteristic curve; those marked *s*, from exposures in the solarized region; while that marked *m* corresponds to an exposure giving the maximum density for shorter times of development. It is clear, therefore, that the effect of solarization is to reduce the developability of the grains but that continued action of the developer overcomes the resistance of the grains and eventually produces metallic silver from all of the exposed grains.

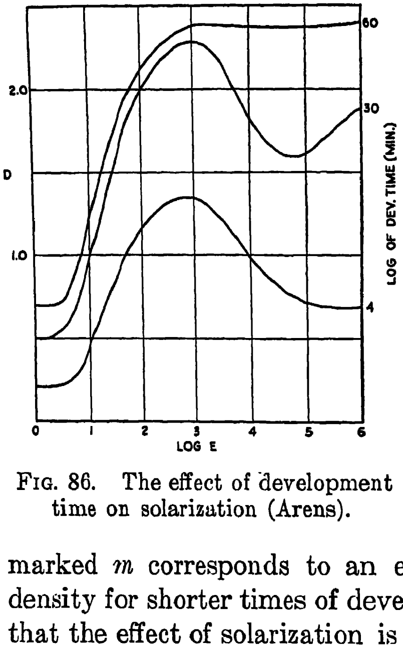

FIG. 86. The effect of development time on solarization (Arens).

Arens[3] studied the relation between the mass of silver per unit area, the number of grains of silver produced after development, and the mass of the individual grains throughout the region of solarization. These measurements were made for both chemical and physical development in the normal and solarized regions. He found that in the case of ordinary chemical development, the optical density, the mass of the silver per unit area, the number of grains of developed silver, and the size of the individual developed grains are less for solarized images than for normal images; that is, for the same time of development, the solarized grains are less developable. For physical development using developers containing silver ions, the loss of density in the solarization region is due only to the smaller number of the grains, the mass of the grains in the solarized region being about the same as in the normal region. The covering power, that is, the ratio of the density to the mass of the silver per unit area, increases in the solarization region for chemical development and diminishes for physical development.

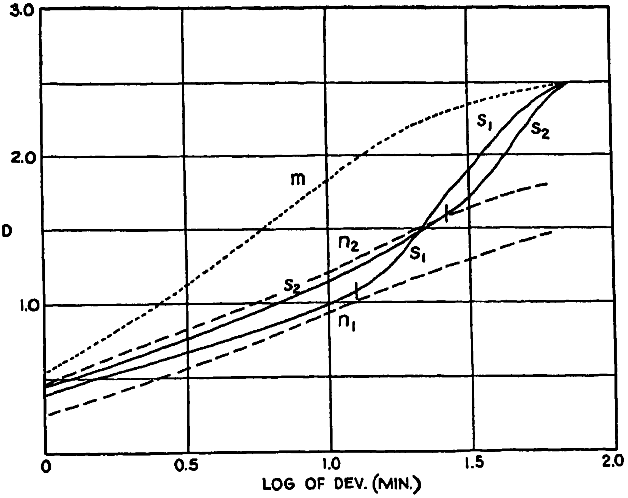

FIG. 87. The relation of density to the time of development in the normal and solarized regions (Arens).

Arens[4] also studied the actual mass of the latent-image silver. In the region where solarization occurs very strongly with physical development and in the region of second reversal, he found that the amount of silver produced by exposure and remaining in the film after fixation without development was greater than for the exposure region where the maximum density could be developed. With physical development, therefore, solarization is not due to a decrease in the amount of latent-image silver. He concluded that in the solarization region the number of developable nuclei diminishes compared with the region of normal development but that the mass of the individual nuclei increases. Moreover, he found that silver solvents destroy the latent image with more difficulty as exposure is increased.

Scheffers[12] showed experimentally with a physical developer and colloidal silver particles in suspension that the rate of growth in size of the particles first increases and then decreases, because the growing particles coagulate to form a coarser, less disperse, modification. This merely shifts the problem to that of the second region of increasing density, which is in disagreement with this explanation of the first reversal. Arens[17] tried to solve the difficulty by assuming that the second region of increasing density does not exist and that it consists only of the increase of density caused by the production of photolytic silver. The reality of the second region shown in the experiments of Lüppo-Cramer and Stenger[18] on plates with peptized silver bromide gel is admitted, but this is regarded as an exceptional case. In 1907 Lüppo-Cramer[19] emphasized the significance of the second region of increasing density.

In an investigation of correlations between different photographic characteristics in the normal and solarization regions of exposure, Trivelli and Jensen[20] could find no correlation between the sensitivity to solarization and the average grain size of their emulsions but did find a correlation between solarization and the silver iodide content of the grains.

Svedberg and Andersson[21] found that the larger grains solarize sooner than the smaller grains. This agrees with Trivelli's[22] measurements on one-grain layer plates and with the covering power of the silver in the solarization region determined by Ballard. On the other hand, Scheffers[12] states that the percentage of the grains which resist development is practically constant in the different size classes. Renwick and Sease[23] found by sedimentation analysis that the larger grains of an emulsion have a higher content of silver iodide than the smaller ones, to which their greater tendency to solarization may be ascribed.

Attempts have been made to account for solarization by two groups of theories: (1) as a development effect or (2) as a purely latent-image effect:

1. Liesegang[5] suggested that a layer of silver so surrounds the silver halide grain in the overexposure region that the developer is prevented from reaching it. The fact that the first reversal of solarization can be obtained after fixation by means

of physical development, as shown by Sterry,[6] Lüppo-Cramer,[7] and Eder,[8] is in disagreement with this theory. According to the gelatin-coagulation theory of Luther,[9] the cause of the first reversal of solarization is a coagulation of the gelatin around the grain by the photochemically liberated halogen, which resists penetration of the developer to the grain. It is difficult on his hypothesis to picture how a re-reversal of solarization by prolonged exposure is possible. In addition, the theory is in disagreement with the fact that solarization also appears in gelatin-free silver halide emulsions, such as collodion emulsions, and even on silver halide plates which are entirely free from any binding material, as shown by Schaum and Braun.[10]

2. The theories which ascribe solarization to the effect of prolonged exposure upon the latent image itself may be divided into those which consider the effect to be due to a coagulation of the image and those which ascribe it to its destruction.

The coagulation effect is supposed to take place as follows: Upon exposure, finely divided silver is produced at the surface of the grain, which is active and is the substance of the normal latent image. Upon further exposure, the silver becomes more compact by coagulation and loses its catalytic properties.

In favor of this theory is the fact that in the region of solarization the total amount of photochemically formed silver does not decrease but increases in proportion to the total amount of exposure. This was shown by Eggert and Noddack,[11] Scheffers,[12] and Tollert,[13] as well as by Arens.[4]

Lüppo-Cramer states, however, that the total amount of photochemically formed silver is not so important to solarization as the distribution of this silver over and in the silver halide grain. Lüppo-Cramer [14] and Silberstein [15] consider that agglomeration should increase the rate of development, and the observations of F. C. Toy and of R. P. Loveland and A. P. H. Trivelli agree with this. Slater Price [16] does not regard this evidence sufficient against the coagulation theory, since the observations may be explained by assuming that amicrons of insufficient size to act as nuclei agglomerate to larger particles.

On the whole, the idea that solarization is due to a coagulation of the latent image does not seem to have sufficient proof.

The possible destruction of the latent image with continued exposure has been discussed by many workers. According to the accepted theory, exposure produces a deposit of silver on pre-existing sensitivity specks on the surface of the silver halide grains of a size that initiates development. It is obvious that solarization, being a diminishing of the developability of the speck, could be ascribed to a decrease of the size of the speck by prolonged exposure. This led to a dispersion theory of the latent image in the solarization region. That light is able to disperse metals was shown by Svedberg, but this metal was dispersed in a liquid, which is different from dispersing particles adsorbed on a silver halide crystal surface surrounded by solid gelatin; on the other hand there are well-established evidences for the coagulation of particles by the action of light.

Renwick[24] suggests that solarization may be due to a peptizing action on the latent image

> ". . . on the part of the later formed chemical products of light action (bromine, hydrobromic acid, etc.) with formation of a photohalide relatively rich in dissolved silver, but almost undevelopable."

Clark's[25] comment on this is:

> "Although there is not yet much evidence in support of this explanation, it is clear that the presence of the silver halide, together with the latent image, is necessary for reversal to occur."

It seems probable that solarization is due to the action on the latent image itself of bromine liberated by continued photochemical decomposition of the silver bromide. Lüppo-Cramer, long before anybody else, urged that solarization should be explained as a regression. He believed that the halogen is liberated within the grain and diffuses through the silver bromide crystals to the surface, where it reunites with free silver. In this way, it would be possible for the total amount of photochemically formed silver in the grain to increase continually; and, at the same time, the silver particles on the surface of the grain might decrease in size, diminishing the developability.

According to present ideas as to the formation of the latent image (Chapter IV, p. 184), the absorption of light in the photographic grain causes ejection of an electron from the energy band belonging to the bromine ions of the crystal into the conduction band. This process leaves one uncharged bromine atom in the crystal. Though bromine atoms themselves cannot diffuse through the silver halide lattice, nevertheless the position of the bromine atom formed in this way must not be regarded as fixed. This is because the vacancy left by the ejected electron can be shifted. A bromine atom may pick up an electron from an adjacent ion, thereby effectively shifting the position of the bromine atom by one lattice point. By repetition of this process, it is possible for a bromine atom formed at one point of the crystal to give rise to a bromine atom at another point in the crystal without the original atom moving at all. By this process, bromine atoms formed at interior points of the photographic grain can transfer to the grain surface, where they are released. This release of bromine atoms prevents any accumulation of negative charges at the surface. Since the release of electrons by light action takes place throughout the grain, the concentration of the latent image at the surface should increase the negative surface charge, but this is compensated by the transfer of the charge to the bromine atoms in the interior of the grain with a release of bromine at the surface.

As long as the exposure is low, the amount of bromine liberated over the grain surface in this way remains small, and the surrounding gelatin medium is an adequately good halogen acceptor to take up all the bromine set free. With high exposures, however, the situation is different: Large amounts of bromine may be liberated, and if the exposure takes place in a short time, high concentrations of bromine may result in the region immediately surrounding the grain surface. Under these conditions, it seems probable that bromine would attack the latent-image specks and form a protective layer of silver halide on their outer surfaces. The latent-image silver specks would become inaccessible to the developer and the grain thereby be rendered less developable.

The rebromination theory of solarization supposes that bromine attacks only that silver formed near the grain surface and not that formed deeper in the grain. Thus, in the solarizing region of exposure, photolytic silver can continue to be formed under the surface.

A number of experiments immediately suggest themselves for testing the rebromination theory of solarization. If exposures are made at different temperatures, the rate of chemical reaction of bromine and gelatin as well as between bromine and silver should be altered, thereby giving rise to observable effects. The addition of bromine acceptors to an emulsion should alter its solarization characteristics. A change in the intensity level at which exposures are made would result in different concentrations of bromine around the grain during exposure and should accordingly affect the degree of solarization. Further, if solarization arises from a coating of silver halide on the surface of the latent-image specks, in accord with the theory outlined, it should be possible by short treatments with silver halide solvents to render the latent-image silver specks available again for development and thus diminish solarization. The above experiments relate to the ordinary chemical type of development. If solarization results from rebromination of the latent-image silver, it should occur also with pre-fixation physical development. Experiments of the type referred to above have been carried out, and some have been repeated many times by different investigators.

In a study by Webb and Evans,[26] a series of exposures was made with the emulsion maintained at temperatures which ranged from 58° C. to −196° C. The results are shown in Figure 88. It is seen that below room temperature, the first effect is a lowering of the maximum density value. As the temperature drops below −73° C., this maximum shifts toward higher exposure values. Both of these effects continue until a temperature of about −100° C. is reached. Below −100° C., the curve rises again and the solarization decreases. At −196° C., a full negative characteristic curve is obtained, with no solarization. Thus, lowering the temperature sufficiently (to −196° C.) eliminates solarization. The great drop with temperature of the negative side of the characteristic curve, as shown by the fall in maximum density, must be attributed in part to the effect of lower temperature on the regular latent-image process through lowering of the silver-ion conductivity of the silver halide grain. However, the very large magnitude of this drop over the range of 25° C. to −100° C. makes it appear probable that part of it may be due to increase of solarization and a shift of solarizing action to the region of the negative side of the curve.

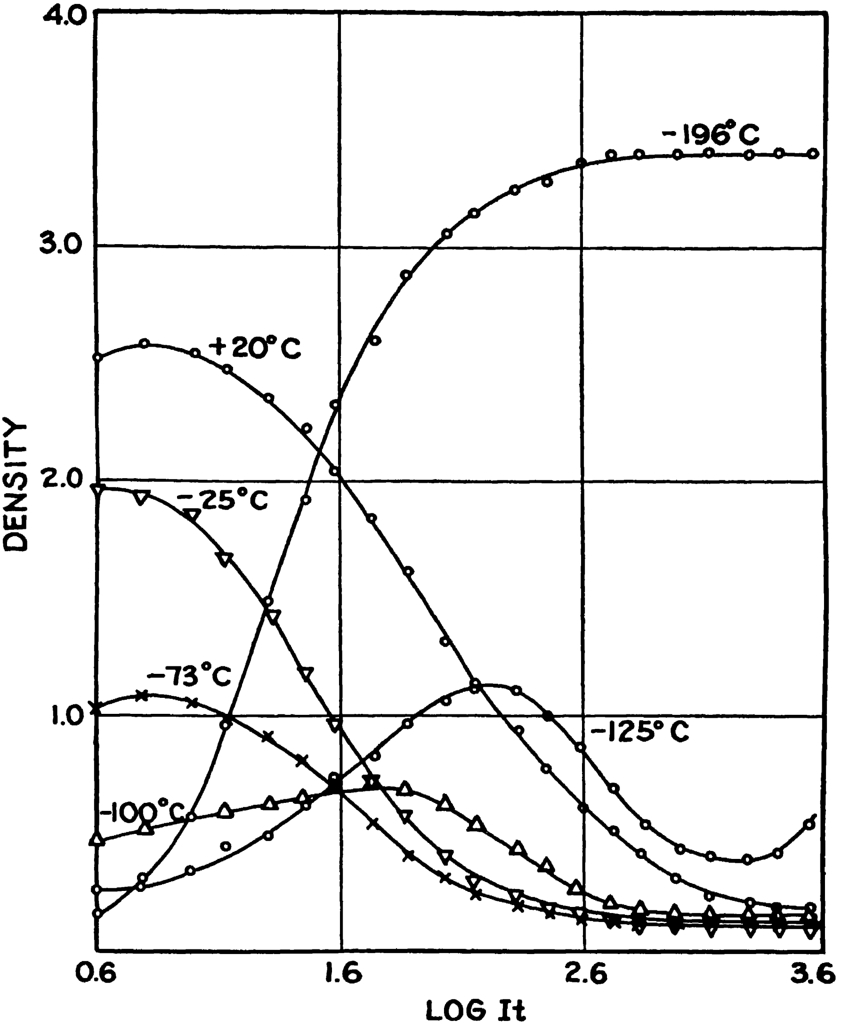

Fig. 88. The effect of temperature upon solarization.

The increase of solarization with lowered temperature may be readily understood on the basis of the rebromination theory. If it is assumed that during exposure gelatin acts as an acceptor for photochemically released bromine, lowering the temperature would decrease the reactivity of the gelatin for the bromine, and a higher concentration of bromine around the grain would be available to attack the latent-image silver specks. Evidence to support this view is found in experiments on emulsions to which bromine acceptors were deliberately added. At room temperature, these emulsions showed no solarization; but if the temperature was lowered, solarization appeared. On lowering the temperature further, however, solarization disappeared, which presumably must be attributed to a lessened reactivity of bromine with the latent-image silver.

The effect of exposure at −196° C. is remarkable not only because of the absence of solarization but because such high densities can be obtained at this temperature. The densities obtained show that practically all the grains of the emulsion have been rendered developable. According to the Gurney-Mott[27] theory of latent-image formation, based on the trapping of electrons at the sensitivity specks followed by silver-ion conduction, it is difficult to understand how this action can take place at such extremely low temperatures. A satisfactory explanation seems to be that given by Berg;[28] namely, that at low temperatures the photographic grain can store up electrons in shallow traps throughout the crystal, and these electrons can be liberated when the temperature of the emulsion is raised for development, permitting the latent-image formation to be completed at a temperature higher than that at which the exposure was made. That the silver halide grain can store up electrons at low temperatures in the manner outlined is confirmed by observations on large single crystals of silver halide at low temperature. Below −100° C., it is found that illumination of these crystals changes them from insulators into semiconductors. This means that electrons are stored in energy levels so closely below the conduction band of the crystal that moderate electric fields suffice to eject them into the conduction band, where they become available for movement through the crystal. If this view is correct, the absence of solarization at extremely low temperatures may be due to no silver being actually formed during the exposure period, when the bromine is being freed. Thus, the bromine liberated combines with gelatin or diffuses away. If the emulsion is warmed, the latent-image silver forms after the bulk of the photochemically liberated bromine has escaped. The rather sudden change in the characteristic curve in the region of $-100°$ C. supports this explanation. Whether the absence of solarization at low temperature is due to the nonreactivity of bromine and silver at low temperature or to the fact that silver is not formed and, therefore, is not available for attack by the bromine at the low temperature is not important for the present discussion. Either mechanism or a combination of them accords with the general rebromination theory of solarization.

Webb and Evans made an analysis of the large and small grains of the emulsion used in their experiments. They found, after fractionation by centrifuging, that the largest grains (2 per cent of the total) had the same silver halide content, in terms of iodide, bromide, and chloride, as the smallest (2 per cent of the total). This eliminates interpretations based upon chemical differences in the halide content of the grains as a function of grain size.

Lüppo-Cramer [29] showed that a solarized exposed silver halide plate after treatment with potassium iodide solution develops rapidly without a trace of solarization. Potassium iodide breaks up the grain crystal into smaller particles by forming silver iodide from silver bromide and would expose developable specks to the developer. (This he termed *Keimblosslegung.*) If a solarized latent image is at the surface of the grain, a normal latent image may be under the surface (Chapter VIII, p. 315).

In addition to iodide, silver halide solvents destroy the solarization effect if the emulsion is treated with them after exposure and before development.[26,30] Thus, in Figure 89 are shown the curves obtained by treatment of a solarized image with water and with a solution containing 16 grams of thiosulfate per liter, the treatment being continued in one case for thirty seconds and in the other for four minutes. Even after one minute's exposure to daylight, the thiosulfate solution greatly reduces the solarization of the emulsion. It is concluded that the dilute thiosulfate solution removes the protective coating of silver bromide formed on the surfaces of some of the development centers produced during the earlier stages of exposure. These centers are, thus, again made accessible to the developer. Treatment prolonged enough to make all the grains developable once more dissolves so much of the silver bromide of the original grains that the maximum density is reduced. In their work on the surface and internal latent images, Berg, Marriage, and Stevens[31] (p. 169) found that no solarization was obtained if the treatment was such that the internal latent image was developed. Sensitometric strips were given a very long range of exposures and

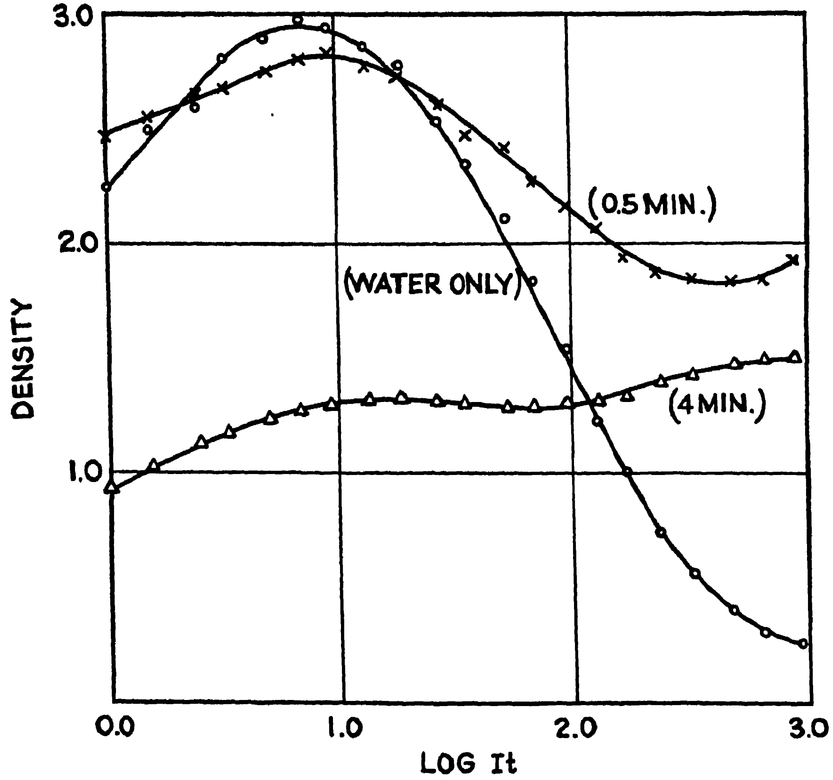

Fig. 89. Result obtained by treatment of a solarized image with thiosulfate solution.

then developed with (*a*) surface developers and (*b*) developers containing silver solvents, before and after treatment with bleaching solutions to destroy the surface latent image. The result shown in Figure 90 is that which would be expected if solarization is due to the rebromination of the latent image by free bromine.

A delay or complete destruction of the solarization effect is produced by the addition of substances which readily accept halogens. Abney [32] observed that the incorporation of reducing agents in the emulsion postponed solarization, and the observation has often been confirmed.[33] The matter was studied by Webb and Evans, whose results are shown in Figure 91. It is seen that a semicarbazide salt diminishes solarization, while acetone semicarbazone destroys it, and *p*-hydroxyphenylglycine* is almost completely effective in inhibiting solarization. While the semicarbazide hydrochloride was not very effective at 25° C., it became so at 58° C. These results may be explained as follows: At 25° C., the bromine acceptors acetone semicarbazone and glycin, if incorporated in the emulsion, have sufficient acceptor action to prevent photolytic bromine from reaching and combining with the silver of the development centers. According to this point of view, the beginning of solarization seen at the high-exposure end of the curve for the emulsion treated with glycin is to be attributed to the exhaustion of the glycin by combination with bromine. Photolytic bromine formed thereafter would be available for rebromination of latent-image silver. Semicarbazide, on the other hand, appears to be a less efficient bromine acceptor at 25° C. than the other compounds. If the emulsion containing it is warmed to 58° C., however, solarization

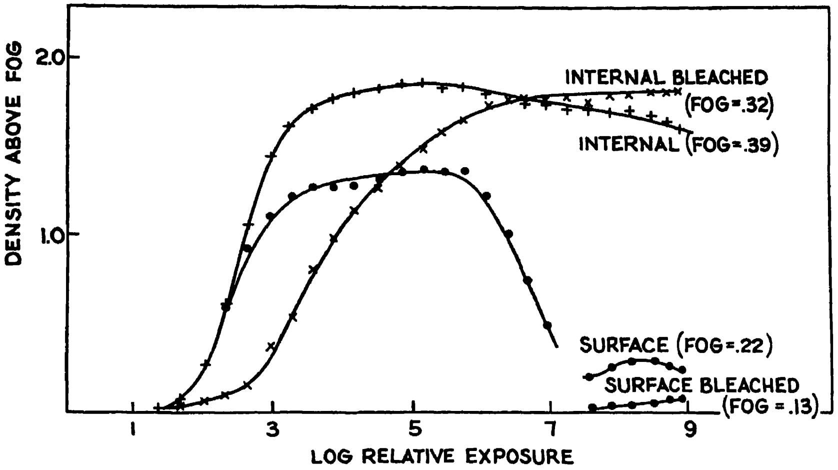

FIG. 90. The solarization of surface developers and those containing silver solvents before and after treatment with bleaching solutions.

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* The developing agent known to photographers as *glycin*.

disappears, indicating an increase in the rate of reaction of the bromine.

If solarization is caused by rebromination of the latent image by halogen liberated during overexposure, exposures made at

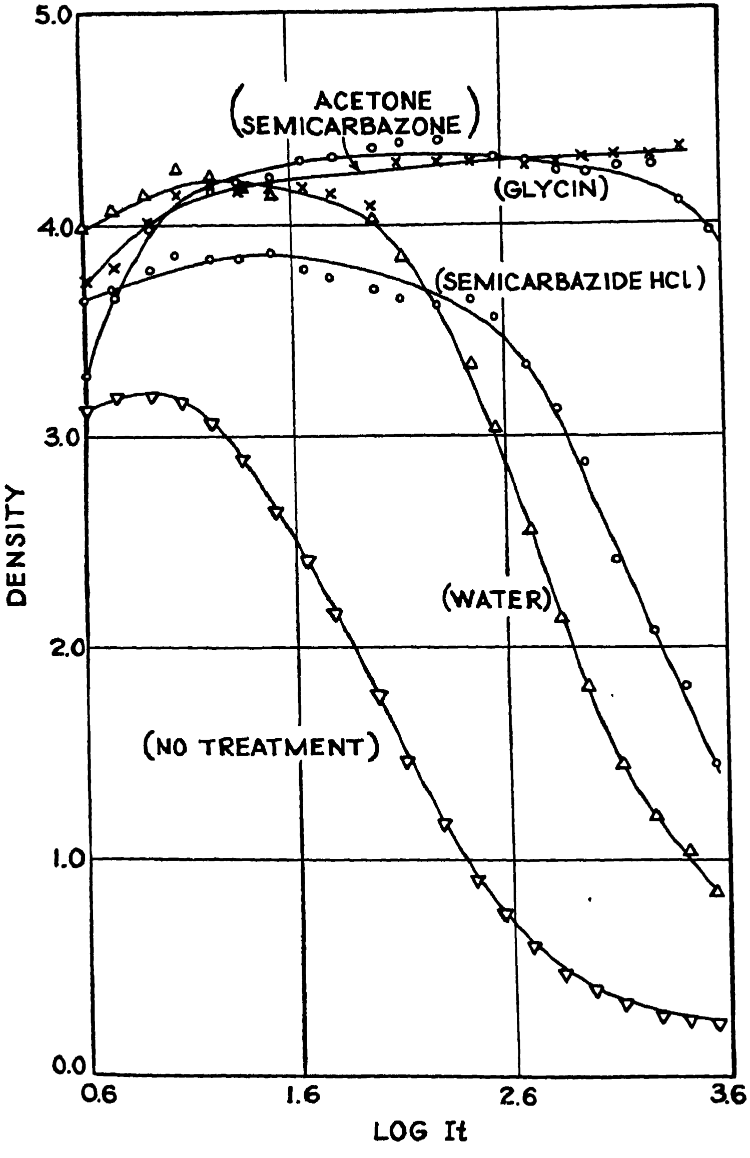

Fig. 91. The effect of halogen acceptors on solarization.

different intensity levels should show different degrees of solarization. The reasoning here is that if an exposure were made at high intensity, the bromine would reach a higher concentration immediately surrounding the grain than if the exposure were made at a low intensity. To test the foregoing hypothesis, solarizing exposures were made by Webb and Evans at two

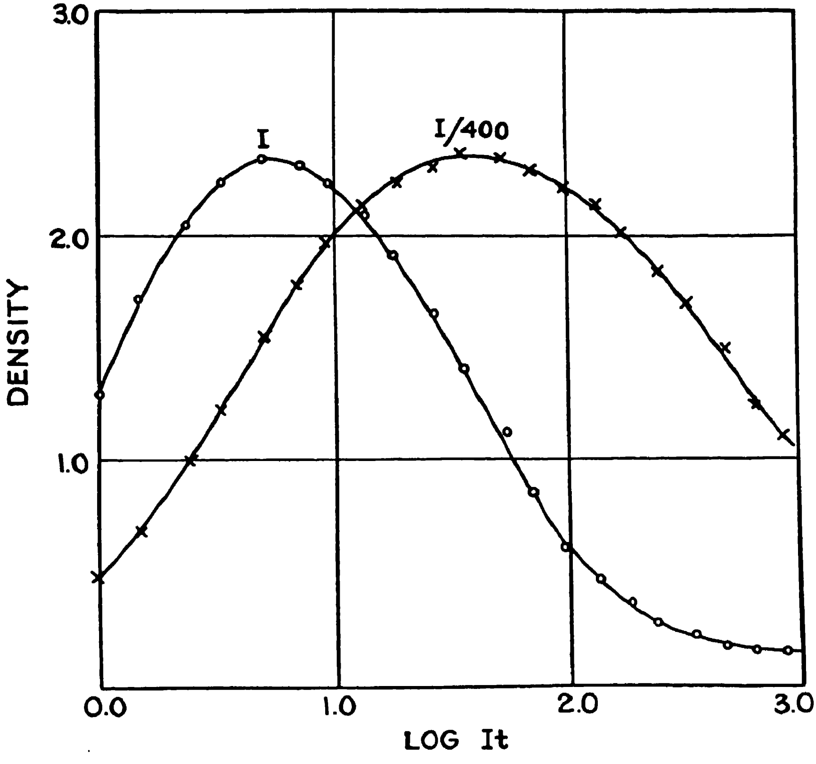

FIG. 92. The effect of the light intensity on solarization.

intensity levels in the ratio 1 : 400. The high-intensity exposure was made with the lamp at 0.6 meter, t = 30 seconds. The times of the exposures were varied reciprocally so that the total exposure in the two cases remained the same. The results are shown in Figure 92, which illustrates that much greater exposures are required to produce the same degree of solarization with the low-intensity exposure than with the high-intensity exposure. There is a shift in the negative side of the curve which may be attributed to reciprocity law failure. However, in spite of this, the shift in the solarized part of the curve has changed by an amount greater in logarithmic units by 0.5. Thus, it appears that the shift in the solarization region with lowered intensity is in the direction to be expected on the basis of the rebromination theory.

As stated above, different emulsions vary greatly in the extent to which they show solarization, and up to the present no explanation of this variation has been given. Methods for preparing emulsions which show great solarization have been published in the papers by Arens [34,2,3,4] and also in various patents. Arens showed that if an emulsion is prepared with an excess of silver and is then peptized with potassium bromide, it will show very little solarization immediately, but if it is digested with an excess of potassium bromide, it will show very strong solarization; and this process is irreversible since treatment with silver nitrate after digestion with excess of bromide does not destroy the tendency to solarization. Bromine ions in the emulsion increase solarization provided they are present during the exposure, and the effect of nitrite, for instance, in decreasing solarization can be reversed by the addition of free bromide. In general, Arens found that an emulsion prepared with an excess of silver (and, of course, afterward adjusted by the addition of potassium bromide) solarizes less than one in which bromide has been present in excess throughout precipitation. A lower minimum density is obtained in the excess of potassium bromide during precipitation, and digestion is increased. Arens could find no definite relation between the distribution of the grain sizes and solarization. Ripening with ammonia greatly increases solarization. It may be said in general, therefore, that emulsions which tend to solarize are those prepared by continued digestion with excess of potassium bromide and, particularly, in the presence of ammonia.

There exist materials on which direct positives can be obtained by simple exposure and development, by their solarization. In some of these, an emulsion is used which, before coating, is fogged either chemically or by radiation to a point which corresponds with the maximum density of the reversal curve.[86] In others, easy solarization is obtained by the addition of a sensitizing dye and a reducing agent to an ordinary negative emulsion.[87] Direct positive emulsions made by this procedure differ from those prepared by fogging in that both negative and positive characteristics are shown by the emulsion. The mechanism of the reversal process for emulsions of this sort may be different from that of the prefogged type. The maximum density and speed are controlled both by the quantity and type of dye added and by the quantity of reducing agent. As the maximum density is increased by adding reducing agent, possible destruction of the latent image by oxidation is indicated.

THE HERSCHEL EFFECT

If an emulsion which has been exposed to blue light is subsequently exposed to long-wave radiation before it is developed, some of the effect of the original exposure is erased. In other words, the red light is capable of destroying to some extent the latent image formed by blue light. This is known as the *Herschel effect* since observations of a similar kind were made by Sir John Herschel in 1839.[35] Herschel, however, experimented on an appropriate paper and found that the visible image was destroyed. Moreover, this occurred in the presence of excess of potassium iodide. Herschel is quoted by Abney:[32]

> "A paper endowed with a pretty high degree of sensibility may also be prepared with the following triple solution, *viz.*: 1st, acetate of lead; 2nd, hydriodate of potash; 3rd, nitrate of silver. . . . If paper so prepared and darkened in the sun be washed over with a fresh dose of hydriodate, the exposure to sunshine being sustained, it whitens with great rapidity; and were it practicable (which I have not found it) to ensure precisely the same ingredient-proportions, and the same degree of blackening in the sun to start from, I should not hesitate to propose this as an excellent process for a positive photographic paper."

Abney points out that the exposure to light of silver iodide in the presence of silver nitrate liberates iodine and that this iodine would bleach the silver produced by the original exposure. The effect actually observed by Herschel, therefore, may have a simple explanation.

Abney himself[36] found that if collodion emulsions of silver bromide or silver iodide are exposed to light, then treated with oxidizing agents, such as potassium bichromate, nitric acid, permanganate, or hydrogen peroxide, and then exposed to the spectrum, the image will be destroyed from the beginning of the red well into the infrared portion of the spectrum. He considered that this represents an acceleration of oxidation by red light.

In 1902, Lüppo-Cramer[37] published a paper in which he expressed doubt that the destruction of a latent image by light of long wave lengths actually occurs on ordinary dry plates, and this was generally believed by other workers at that time, probably because the plates made then did not show the effect to any marked extent. Many photographic materials show the Herschel effect to only a small extent.

Millochau,[38] however, photographed the infrared spectrum of the sun by the use of the reversal effect, and after this there remained no doubt as to its existence. He assumed (without adequate proof) that the pre-exposure penetrated into the depth of the emulsion, while the infrared after-exposure was active only in the surface. He therefore treated his emulsions with dyes which absorbed the actinic part of the spectrum and transmitted the infrared. Malachite green was especially effective. In this way, he obtained exposures up to the limit of transmission of his apparatus, about 800 mμ.

In 1910, Volmer[39] found a reversal of density without the use of dyes. He established that the plate is again sensitive to short wave length light after reversal by infrared light, and that solarized places on the plate can be blackened by infrared light. In further work by Volmer and Schaum[40] and Schaum and Langerhanness,[41] attempts were made to show the relationship between the Herschel and other photographic reversal effects, such as the Clayden and Villard effects.

In 1923, Terenin[42] published the results of experiments carried out in much the same way as those by Millochau. He used dyes in much lower concentrations and recognized that the results could not be explained merely by filter action protecting the emulsion from blue light. The triphenylmethane dyes—iodine green, malachite green, and brilliant green—were the most satisfactory. The long wave length limit of the reversal effect was uninfluenced by the dye but the short wave length limit varied.

Arens[43] in 1925 confirmed the observation of Lüppo-Cramer that the reversal effect by long-wave radiation is dependent upon the presence of potassium bromide. Arens assumed that the Herschel effect is due to an oxidation of the silver nuclei by bromine controlled by the concentration of bromide ions.

In 1926, Leszynski[44] made an extensive study of the Herschel effect and pointed out that much of the previous work was inaccurate because the light used in making the infrared exposure contained a certain amount of actinic light. Using a combination of filter, light source, and emulsion such that in the longest infrared exposures there was no forward action, he found that infrared exposure causes a reversal of the density produced by light, X rays, alpha rays, or hydrogen peroxide, for both ordinary chemical development and post-fixation physical development. No reversal was found in the direct print-out effect with the pure silver bromide emulsion used by Leszynski. The magnitude of the reversal effect was independent of the wave length of the pre-exposing actinic light and for equal energy independent of the intensity of the infrared exposure for variations of intensity over the range 75 : 1. However, the Herschel effect was found to vary with the intensity of the pre-exposure, the reversal effect decreasing with lower intensity level. Leszynski came to the conclusion that the oxidation theory of the Herschel effect is doubtful. The experiments of Lüppo-Cramer[45] in which reversal occurred in the presence of sodium nitrite also offer evidence against it.

As an alternative to the oxidation theory of the Herschel effect, Leszynski put forward a hypothesis based on a redistribution of, or dispersion action on, the latent-image silver nuclei by the infrared exposure. According to this view, the amount of silver contained in the nuclei remains constant during the infrared exposure, but a redistribution takes place. Leszynski suggested that this action could take place by the ejection of electrons from silver atoms lying on the surface of nuclei and their removal to distant silver ions to form silver atoms in a new position. This physical dispersion theory of the Herschel effect has received support from other workers on the subject. Tollert[13] in a study of the action of red light on photolytically formed silver found that infrared exposure produced no measurable alteration of the amount of silver, from which he concluded that the Herschel effect is to be viewed as an alteration in structure, probably a dispersion, of the latent-image silver. Tollert compared the energy of the blue radiation, which produces a definite developable density, with the amount of energy in the infrared which reverses this density. He found that the action of $10^{9\pm 1}$ quanta of red radiation is required to undo the action of one quantum of blue radiation.

Trivelli[46] in 1929 carried out a quantitative investigation of the Herschel effect to determine the influence of the amount of exposure both to blue light and to infrared. He found that the Herschel effect, expressed as the ratio of the reversed density to the initial density, reaches a maximum at some intermediate value of pre-exposure. Also, the time of development influences the amount of the Herschel effect to a small extent. Trivelli concluded that all materials which desensitize for the latent-image process sensitize for the Herschel effect.

In further work, Trivelli and Hall[47] attempted to establish a connection between the Herschel effect and the reciprocity law failure. By applying the same infrared after-exposure to the latent image formed by pre-exposure, using three different intensities, varying amounts of reversal were obtained. Contrary to the results obtained by Leszynski, strong Herschel effects were observed if very weak intensities were employed in the pre-exposure to blue light. A result of further interest is that the maximum Herschel effect shifts to lower densities as the intensity of the pre-exposure is lowered.

Carroll[48] showed that, in the presence of desensitizing dyes, reversal might occur throughout the visible spectrum or even into the ultraviolet, as well as in the red or infrared. His spectrograms indicate that the region of reversal is related to the absorption of the dye. Narbutt[49] in 1930 also obtained reversal with short wave length radiation. If the view advanced by Leszynski that the Herschel effect is due to a dispersion of the latent-image nuclei by the action of the secondary exposure is correct, the logical conclusion is that the short wave length light can disperse the silver nuclei of the latent image just as the long wave length light can. The reason that the short wave lengths do not have a reversing action on untreated plates is that the forward action of these rays on the plate far outweighs their reversing action.

Mauz[50] found, in agreement with Carroll and Narbutt, that reversal could be obtained by short wave length radiation on plates which had been desensitized with dyes (Chapter XXIV, p. 1040). Mauz worked with pinakryptol yellow, pinakryptol green, fuchsin, and phenosafranin. With all of these, he found an enhanced reversal effect in the red and infrared regions where the ordinary Herschel effect is observed. In addition, he found reversal to some extent at all wave lengths throughout the visible spectrum and an especially strong reversal band in the blue region, with a maximum at about 420 mμ. Mauz failed to correlate the spectral sensitivity of the reversal effect with the spectral absorption of the desensitizing dyes.

Carroll and Kretchman[51] in 1933 carried out a series of experiments on photographic reversal and desensitizing dyes. They studied the relationship between the spectral sensitivity of the reversal effects and the spectral absorption of the dyes. However, instead of measuring the absorption curve of the dyes in solution, they determined the absorption curve of the dyes adsorbed to the silver halide surface and compared this with the density curve of the reversal effects. In this way, they were able to show a correlation between reversal and absorption of energy. At least in the region of the maximum dye absorption, a band of strong reversal was found in all cases. The desensitizing dye did not appear to increase the original Herschel effect of the untreated plate but added to it the effect of reversal in other regions. In agreement with Mauz' work, these workers found a strong reversal band in the blue region of the spectrum and a maximum at about 420 mμ corresponding to the absorption of the silver halide. They concluded that these experiments supported the oxidation theory of the reversal by desensitizing dyes.

Blau[52] provided further evidence that oxidation is the major process in reversal with desensitizers. When the second exposure was carried out at 6 cm. pressure, reversal in plates treated with pinakryptol yellow was almost eliminated. Similarly, in plates treated with capri blue, reversal in red light was replaced by sensitization if the oxygen pressure was reduced. Control experiments showed that vacuum does not have any effect on normal image formation. On the other hand, the presence of oxygen in the absence of desensitizers does not seem to affect the Herschel effect. This was carefully tested by Thurston and Blair,[53] who found no measurable difference between air, hydrogen, and oxygen when using motion-picture positive film, bromide paper, and chloride paper.

The chief evidence in favor of the oxidation theory is derived from experiments using dyes and other materials, such as bromide, which act as desensitizers for the production of the latent image and enhance the Herschel effect. It has been argued, however, that the action of desensitizers is to stop the forward action and thus enhance the effect of the after-exposure to red light. Undoubtedly, some of the action of desensitizing materials on the true Herschel effect in the red end of the spectrum can be accounted for in this way. However, it seems doubtful if the part played by the desensitizer on the reversal effects obtained in the *visible* parts of the spectrum can be so explained. The work by Carroll and Kretchman, which shows a strong reversal band agreeing in wave length with the absorption band of the dyes adsorbed to the silver halide, indicates that the desensitizing dyes have a primary role in the reversal action. However, since these workers found a reversal effect also in the infrared and other parts of the spectrum where no absorption by the dye exists, it appears that two types of reversal phenomena may take place, one of which is due to an oxidation process conditioned primarily by the light absorption of the desensitizing dye and the other, a reversal effect due to a direct action of the light on the latent-image nuclei. The latter reversal effect would normally be aided by the use of desensitizers in that any forward action in the second exposure would be eliminated.

In view of the above discussion, it appears best to assume that the action of desensitizing dyes is a complicating factor in the Herschel effect and that it is by no means certain, from the experiments that have been carried out, that the reversal effect obtained with such dyes is identical with that obtained with red light, ordinarily referred to as the Herschel effect. In the remainder of this discussion, the Herschel effect will be treated as consisting merely of reversal which takes place under the action of red or infrared light. The experiments with desensitizing dyes have been described because they are so intimately bound up with the study of the Herschel effect.

Some very important results on the Herschel effect have been obtained through the work of Urbach and Wolinski[54] in 1938, in which blue and infrared light exposures were given simultaneously. The reversal effect obtained by the simultaneous action of infrared and blue light was first studied by Lüppo-Cramer,[55] who called it the "intermediate Herschel effect." By a quantitative study of the action of infrared and blue light with exposures applied simultaneously and successively, Urbach and Wolinski showed that if the infrared exposure was applied simultaneously with the blue light, it produced a greater effect than if applied successively. They considered that this is due to a delay in the stabilization of the latent image and that if the infrared dispersing exposure is applied to the latent image before it is stabilized, it is much more readily destroyed than if the exposure is applied later. This view was supported by further experiments in which the time between the pre-exposure to blue light and the subsequent infrared exposure was varied. It was found that the reversal action is lessened with increasing time between the two exposures. These results are in accord with the view that the Herschel effect is due to a dispersing action, as outlined by Leszynski, and that the silver nuclei can be broken up more readily during their formation while they are still unstabilized.

Studies of the spectral distribution of the Herschel effect have been carried out by Gorokhovskii and Shestakoff[56] and by Bartelt and Klug.[57] Gorokhovskii and Shestakoff studied the spectral distribution of the Herschel effect as a function of the density, D_0, produced by the pre-exposure to blue light and found that the wave length which at small D_0 produces a forward action may at higher values of D_0 destroy density. With an increase of D_0, the Herschel effect was found to increase and the maximum of the activity as a function of wave length to shift toward shorter wave length. These workers found that desensitizing with potassium bromide causes a uniform reduction of emulsion sensitivity over the entire spectrum and, at the same time, a sharp increase of the Herschel effect in the red with a shift of the maximum toward shorter wave length. They postulated that in exposure to red light there are two processes: a forward action consisting of formation of latent image and a reversal action bringing about destruction of the latent image. They thus attribute the increase of the Herschel effect to a suppression of the forward component of the red-light exposure.

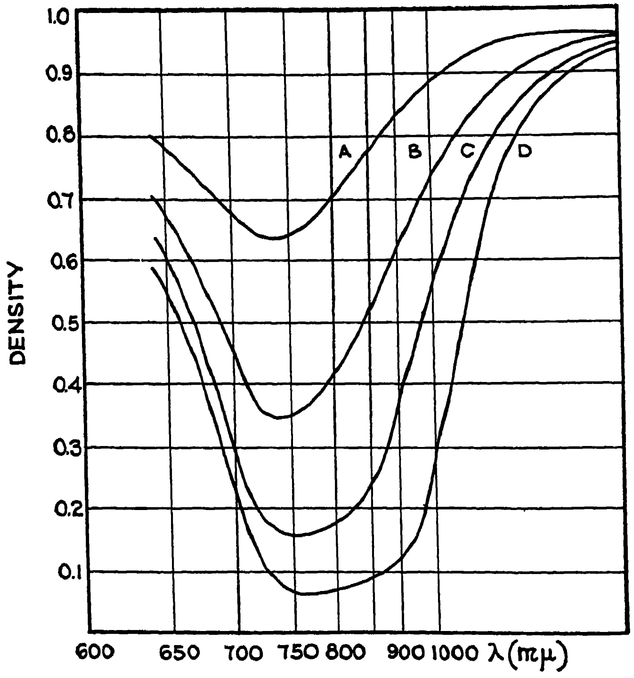

FIG. 93. The Herschel effect as a function of the wave length of the reversing radiation.

The Herschel effect as a function of wave length of the reversing radiation is shown in Figure 93, from the work by Bartelt and Klug. These curves show the decrease in density resulting from the red-light exposure, and the different curves *A*, *B*, *C*, *D* correspond to increasing amounts of red-light exposure. An important feature is the shift of the maximum of the Herschel effect toward longer wave lengths with increasing red-light exposure. If the dispersion theory of the Herschel effect is correct, this indicates that the more dispersed the latent-image nuclei and, therefore, the smaller they are, the less energy is required to break them up further. This is in qualitative agreement with the results of Gorokhovskii and Shestakoff, who found that with increasing values of pre-exposure density (larger latent-image nuclei), the maximum of the Herschel effect shifts toward shorter wave lengths. From these results, the indications are that the wave length of the reversing radiation varies inversely with the size of the latent-image nuclei.

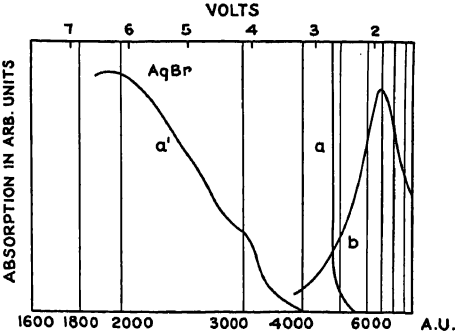

Fig. 94. The absorption bands of silver bromide (Hilsch and Pohl).

Important information relative to the nature of the Herschel effect has been obtained by studies carried out on large single crystals of silver halide. It is well known that the silver halides develop a coloration when exposed to light absorbed in their characteristic absorption bands. Hilsch and Pohl[58] found that the coloration in large single crystals of silver bromide is due to an induced absorption band with its maximum at 700 mμ. In Figure 94 are given curves from Hilsch and Pohl's paper showing this induced absorption band *b*, and the characteristic absorption band of silver bromide *a'*. The curve *a* corresponds to curve *a'* multiplied by a factor 10^6 to put it on the same scale as curve *b*. In their studies of this absorption band, Hilsch and Pohl kept the concentration of photo-product at about the same level as in the normally exposed photographic emulsion. They found that if a crystal previously colored by exposure to light is exposed to longer wave length light falling within the induced absorption band, this band is bleached, and preferentially so in the wave length region of the bleaching light. Hilsch and Pohl suggest that the induced absorption band produced by the short wave length radiation corresponds to the latent photographic image and that the bleaching of this band by long wave length light corresponds to the Herschel effect in the photographic case. The great width of the induced absorption band in single crystals and its nondependence upon temperature were interpreted to mean that it arises from colloidal particles of silver of a great variety of sizes, each particle size having its own absorption band. It appears that this is substantially correct, but the mechanism by which light is absorbed by the particles leading to their destruction is still not understood. It has been suggested that it takes place through absorption of the classical resonance type by the metallic particles. For the larger colloidal particles of silver dispersed in silver bromide and silver chloride, there is evidence [59] that this is probably correct, but for particles of the size of the latent-image specks, the theory of resonance absorption does not fit the observed facts. This is discussed by Berg,[60] who points out that the dimensions of the latent-image specks are such that they could not possibly resonate with light of the wave length absorbed.

A more likely explanation of the absorption by silver specks of latent-image size is that proposed by Gurney and Mott.[61] They attribute the absorption of long wave length light to the photoelectric ejection of electrons from the silver into surrounding silver bromide. To account for the destruction of the speck in the Herschel effect, it is assumed that a positive silver ion is pushed after the electron by the positive charge left on the speck. The fact that the photoelectric effect would be little influenced by temperature would account for the nondependence of the position of the absorption band upon temperature. To account for the breadth of the absorption band, it must be assumed that the energy required to eject electrons from a small metallic speck is a function of the size and shape of the speck. It is not unreasonable that this is the case with these small particles. The results of Gorokhovskii and Shestakoff and of Bartelt and Klug, which indicate that the wave length of the reversing radiation varies inversely with the size of the latent-image nuclei, support this view. If the absorption process consists of an internal photoelectric effect, *i.e.*, the ejection of an electron from the conduction band of the silver into the silver bromide, it is readily conceivable that the energy required might be smaller, the smaller the number of atoms in the silver speck.

Further experimental evidence [28,62] which seems to support the foregoing explanation of the Herschel effect has been obtained by measurements under varied temperature conditions. Some of these experimental results are shown in Figure 95. The straight horizontal line represents the density obtained on an emulsion by a primary flash exposure to white light. The points indicated with circles represent the density values obtained from a subsequent exposure to infrared light superposed on the primary exposure. The abscissa values are the logarithms of the exposure to the infrared light. The curves of Figure 95*a* show the normal Herschel effect where both white-light and infrared exposures were made at room temperature (20° C.). In Figure 95*b*, the white-light exposure was made at 20° C., and the infrared exposure was made after the emulsion was cooled to −186° C. No Herschel effect was obtained under these conditions. Figure 95*c* shows the results of an experiment in which the white-light exposure was made at −186° C. and the infrared exposure after the emulsion was warmed to 20° C. The Herschel effect was obtained again in this case. Figure 95*d* shows the results of two experiments. In each, both exposures were made at −186° C. However, in the one case the emulsion was warmed to 20° C. between the primary white exposure and the infrared exposure, while in the other the emulsion was maintained at −186° C. between exposures. It is seen that if the emulsion

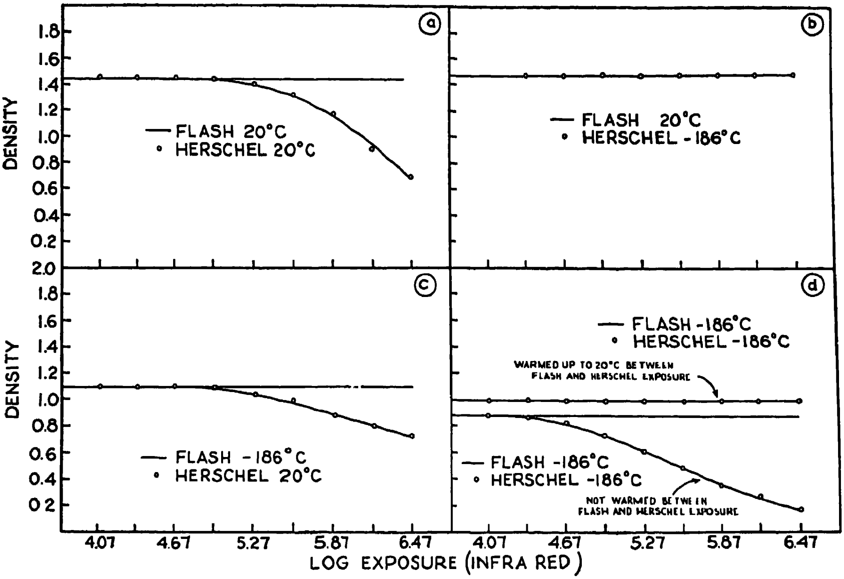

Fig. 95. The effect of temperature on the Herschel effect.

was not warmed between exposures, a large Herschel effect was obtained, while if the emulsion was warmed between exposures, no Herschel effect was obtained.

The foregoing experimental results support Gurney and Mott's suggestion that the destruction of the latent-image speck is due to the ejection of electrons followed by diffusion of a Ag^+ ion. The experiment made at room temperature (Figure 95*a*) has no appreciable bearing on the matter, but it is not discordant with the idea. The results of the other experiments can be accounted for by the proposed mechanism on the assumption that no Ag^+-ion diffusion can occur at −186° C. Thus, in Figure 95*b*, the normal latent image is formed by an exposure at room temperature. In the exposure to the infrared light at low temperature, it is assumed that the electrons are ejected, but if Ag^+ ions cannot follow, the speck will not disintegrate and the electrons will be drawn back again by the positive charge on the speck. Thus, the speck will remain intact after withdrawal of the infrared stimulus. The results of the experiment of Figure 95*c* are very much like those of Figure 95*a*. The Herschel exposure made at room temperature can diminish whatever latent-image nuclei are present. The experiments of Figure 95*d* afford perhaps the most decisive evidence of all. In line with the original assumption of no Ag^+-ion diffusion at −186° C., it must be supposed that the true latent image is not formed by the white-light exposure at this temperature. Instead, only the electronic part of the process will occur, and the resulting condition is a potential latent image consisting of electrons trapped on the preexisting sensitivity specks. If a subsequent infrared exposure is given while the emulsion is still at the low temperature, this potential latent image is readily destroyed. Presumably, this occurs by ejection of the electrons from the speck. On the other hand, if the emulsion is warmed to room temperature after the white-light exposure and before the infrared exposure, the full latent-image specks form. Then, upon cooling the emulsion to −186° C., the latent image cannot be erased by the infrared radiation for the reason applying to Figure 95*a*. These experiments support Gurney and Mott's suggestion that the Herschel effect consists of a primary (photoelectric) and secondary (electrolytic) process. The former is apparently independent of temperature, while the latter is dependent on temperature.

Summarizing, it may be said that two main theories have grown up to account for the Herschel effect:

The first attributes it to an oxidation of the silver nuclei of the latent image by oxidizing agents excited by the exposure to red light. The principal evidence for this theory is derived from experiments using desensitizing dyes and other reagents which render the emulsion insensitive to the forward action of actinic light. In this way, reversal may be materially increased and may be produced by radiation extending throughout the visible spectrum. However, it is doubtful that the reversal effect obtained under these conditions is identical with that caused by infrared light alone on the untreated emulsion, which is usually referred to as the Herschel effect.

The second theory attributes the effect to a dispersion or some other physical alteration of the latent image-nuclei by the direct action of infrared light. Leszynski first put forward this idea, and it has received support from a number of later workers, particularly Hilsch and Pohl, who worked on the coloration and bleaching of large single crystals of silver halide. Gurney and Mott have elaborated the dispersion hypothesis further. They propose a concrete mechanism for the process. The breaking up of the speck is attributed to the ejection of an electron from the silver nuclei by the absorption of a quantum of infrared light, followed by the loss of a silver ion. The ion is supposed to be pushed after the electron by the excess charge on the nuclei. If the electron is then trapped at another point in the crystal, a silver ion will be attracted to this point and a silver atom formed, as described for the formation of the latent image. In this way, an infrared exposure can lead to the breaking up of the original silver nuclei present. Evidence to support the theory of the Herschel effect proposed by Gurney and Mott comes from experiments at low temperature. The effect appears to consist of two parts: a primary electronic part independent of temperature and a secondary ionic process dependent upon temperature.

THE SABATTIER EFFECT

If a film which has been exposed, developed, and washed, but not fixed, is given a second uniform exposure and developed again, a reversal of the original image will be obtained. This effect was discovered by Sabattier [63] in 1850 and is known as the *Sabattier effect.* In the same year, Seely [64] advanced an explanation for the phenomenon based on a simple printing effect. He suggested that the negative image produced by the first exposure and development was printed on the underlying emulsion by the second exposure. Depending upon the magnitude of the second exposure, the reversal may be complete or may occur only in the region where the first exposure is very light. Later work by Stolze,[65] Miller,[66] and Trivelli [67] showed that the Sabattier reversal can be obtained also if the second exposure is given from the back of the plate, and this threw doubt on Seely's explanation. Channon [64] carried out similar experiments by means of crossed wedges and obtained similar results. He showed further that the effect could be obtained also by chemical fogging. A series of carefully executed experiments by Stenger [68] seemed to bear out Seely's original explanation.

An alternative explanation of the Sabattier effect proposed by Seemann [69] is that the bromide liberated during the first development restrains the second development and that this restraining action is proportional to the amount of density in the first image. Serious objection to this explanation is suggested by experiments of Lüppo-Cramer [70] and Leiber,[71] who show that the reversal will be observed if the plate is thoroughly washed after the first development.

Another explanation of the Sabattier effect is that the oxidation products of the first development act as desensitizers for the second exposure. Thus, where the original density is high, more oxidation products result, giving greater desensitization. This explanation was supported by Leiber. However, Lüppo-Cramer [72] and Stevens and Norrish [73] have demonstrated that the Sabattier effect can be obtained with hydrogen peroxide and hydrazine developers which do not form oxidation products.

Marriage [74] suggests that the movement of iodide may be a contributing cause of the Sabattier reversal in iodo-bromide emulsions. It was shown by Dundon and Ballard [75] that in development of an iodo-bromide emulsion, the iodide liberated from the developing grains replaces bromide in the undeveloped grains. Marriage considers that this may cause desensitization of the undeveloped grains. However, experiments carried out by Marriage and by Stevens and Norrish[76] with pure silver bromide emulsions showed that the effect of the iodide can be of only secondary importance.

Marriage made quantitative experiments to determine to what extent the effect could be explained as a purely screening effect, as originally suggested by Seely. As mentioned above, this explanation had been discredited by the fact that the reversal could be obtained if the second exposure was given from the back of the plate. It had not been definitely proved, however, that the blackened image, distributed, as it is, through the depth of the emulsion, does not affect the second exposure even if made from the back side. To test this point, Marriage,[77] following a suggestion of E. R. Davies, used a plate with a light-absorbing dye to confine the light action to the surface. Under these conditions, a normal Sabattier effect was obtained if the second exposure was given from the front side of the plate, but none if it was given from the back. This indicated that the effect might be due to a screening effect alone. To investigate the problem quantitatively, experiments on dyed films were made by means of crossed wedges and the results compared with those computed on the basis of the second exposure being screened by the original image. The film was first exposed through a step wedge, developed, and washed. While still wet, a second exposure was made through the wedge turned ninety degrees from the former position. Two curves were plotted—one, Δ_1, giving the density values due to the first exposure alone and one, $\Delta_{1,2}$, giving the density values of the combined exposures—each plotted as a function of the logarithm of the first exposure. These are shown by the circles in Figure 96. The curve, $\Delta_{1,2}$, represented by the crosses is the calculated density curve for the combined exposures obtained as follows:

Let the density values of the first exposure alone be designated by Δ_1, then

$$\Delta_1 = D_1. \tag{1}$$

The density values of the second exposure alone can be expressed as a function of the second exposure, thus

$$\Delta_2 = f(\log E_2). \tag{2}$$

The densities of the combined exposures, designated by $\Delta_{1,2}$, are represented by the equation

$$\Delta_{1,2} = D_1 + f(\log E_2 - D_1). \tag{3}$$

This should predict the correct shape of the combined exposure curves if there is no effect other than a screening of the second exposures E_2 by the densities D_1, as indicated by the second term. Values of the second term can be read directly from the experimental curve (2), which shows the variation of density with exposure for the second exposure. Fog values are omitted in the above equations in order to simplify the analysis, but the fog terms were included in the calculation of the theoretical curve. The agreement between the observed and calculated curves is good, especially when allowance is made for the fact that the optical density of a silver image is greater when wet than when the second exposure is made. Thus, a reversal of the order of magnitude ordinarily observed in the Sabattier effect can result from a screening effect alone, and Marriage concludes that the optical screening effect is sufficient to account for the Sabattier reversal. Later work by Stevens and Norrish,[78] however. indi-

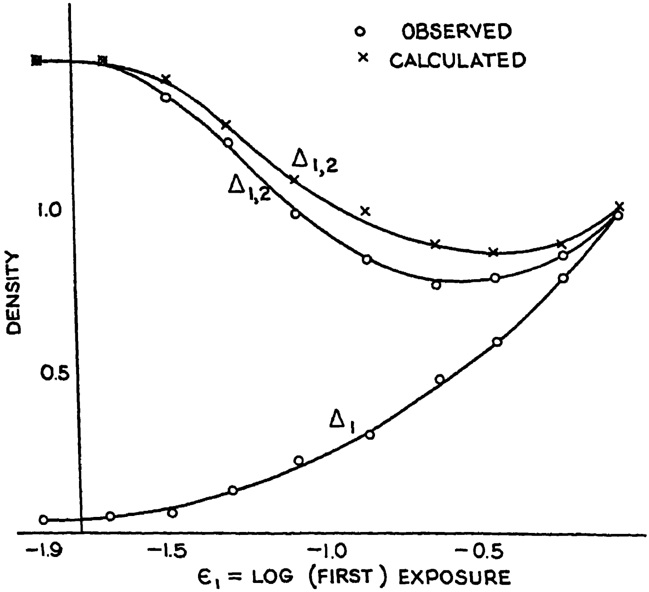

FIG. 96. Curves illustrating the Sabattier effect as produced by screening.

cates that, in addition to the screening effect, there is an effect arising from desensitiztion by the first exposure and development.

The first experiment carried out by Stevens and Norrish was of the same type as that of Marriage and Davies, the second exposure being given from the back of the plate. Instead of using a dye to confine the light action to the surface of the emulsion, these workers used very short first development, so that the developed image was confined to the surface. When carried out in this way, reversal was obtained when the second exposure was given from either the front or back of the plate, though the data show that the reversal action was considerably greater if the second exposure was given from the front. As pointed out by Marriage, these results include, in addition to the effective desensitization due to development, an apparent reduction of sensitivity due to the first exposure. This latter effect constitutes the main part of the whole reduction in sensitivity and should be eliminated before comparing the results in the two cases of exposure from the front and back. If this were done, a still greater difference in reversal effects in the two cases would undoubtedly appear. The experiment in itself cannot be considered as decisive as the one carried out with dye, since the second exposure may be materially affected by the layer of silver deposit on the front surface. A better test, perhaps, would be one made with ultraviolet light to restrict the exposures to the emulsion surface.

Other experiments carried out by Stevens and Norrish were much more conclusive in showing that an effect in addition to screening occurs. In these, instead of light for the second exposure, they used treatment with a sodium arsenite solution and heat treatment up to 100° C. In both instances, there could be no screening effect, and yet distinct reversals were obtained. These results must, therefore, be considered good evidence that a differential desensitization is produced by the first exposure and development.

To test the theory that the Sabattier effect is produced by soluble halides liberated in the first development, pure silver bromide emulsions were used, these being subjected to prolonged washing after the first development. The Sabattier effect was still obtained under these conditions.

To test the theory that oxidation products of the first development are responsible for the desensitization, hydrogen peroxide and hydrazine were used as developers, and a clear Sabattier effect was found. It was concluded that oxidation products are not responsible for the effect.

From their exhaustive series of experiments, Stevens and Norrish concluded that none of the theories advanced previously was adequate to account for the Sabattier effect. They were thus led to suggest that metallic silver liberated during the first development is responsible, that it diffuses from the developing grains to the adjacent grains, and that this deposition of silver on a partially exposed grain produces desensitization. They assume that the silver on undeveloped grains supplies nuclei at which photo-product can coagulate during the second exposure. Increase in the number of nuclei in this way introduces competition among them for acquiring developable size, which leads to lowered sensitivity. To test the idea that metallic silver can diffuse through the emulsion during development, a plain gelatin coating was placed in contact with a developing process plate. By subsequent physical development of this plain gelatin layer, a reproduction of the image of the process plate was obtained. This experiment shows that there is some diffusion of metallic silver through an emulsion during development.

It may be concluded that the Sabattier effect results partly from a physical screening effect produced by a simple printing of the image from the first exposure and development onto the underlying silver halide, and partly from a chemical desensitizing effect resulting from the first exposure and development. The extensive experiments carried out by Stevens and Norrish throw considerable doubt on the theories based on the effect of soluble halides and oxidation products arising from the first development. Their new theory of the effect, based on desensitization by metallic silver, is supported by experimental evidence, but further work on the subject is required.

THE ALBERT EFFECT

In 1899, Albert found that if a collodion plate is exposed very fully, treated with nitric acid, washed, and re-exposed to diffuse light, a reversed (positive) image will be obtained after development.[79] This is known as the *Albert effect.* Lüppo-Cramer [80] showed that this result could be obtained on silver bromide gelatin plates with a solution of chromic acid or ammonium persulfate. He explained this effect as due to partial removal by the chromic acid of the latent-image silver formed in the first exposure.

Lüppo-Cramer made the following observations relative to the Albert reversal: (1) The first exposure must be heavy but not necessarily produce solarization; (2) the Albert reversal seems to be a phenomenon different from solarization because it occurs in emulsions containing sodium nitrite, where solarization is not found; (3) the effect is obtained with the chemical developers hydroquinone, metol hydroquinone, and ferrous oxalate, and with pre-fixation physical development; (4) developers containing silver bromide solvents, such as sodium sulfite, develop a negative image, corresponding to the original exposure, instead of the reversed image. Lüppo-Cramer attributes this to the laying bare of sub-surface nuclei by the solvent action of the developer; (5) no effect is obtained with post-fixation physical development or chemical or physical development after iodization. To explain these results, Lüppo-Cramer referred to experiments on synthetically prepared photo-halides containing varying amounts of silver, in which photo-bromides were the more readily destroyed by oxidizing agents, the more silver they contained. He concluded, therefore, that only a small amount of silver could be occluded as an insoluble photo-halide in the photographic grain. If this amount of silver is exceeded by that produced during the first exposure, the attack on the ripening nuclei of the grain will be facilitated. Only the surface nuclei can be destroyed in this way, and, therefore, if the surface of the grain is dissolved after the chromic acid treatment, the inner nuclei will become available as development centers.

This explanation of the action of chromic acid on exposed grains accords with some results obtained by Clark,[81] who made a quantitative study of the effect of chromic acid treatment on exposed and unexposed emulsions without specific reference, however, to the Albert effect (Chapter IV, p. 151). He concluded that the first exposure makes the sensitivity centers more susceptible to attack by the chromic acid. This view is supported by Sheppard [82] and Lüppo-Cramer.[83]

From some preliminary experiments on the Albert reversal carried out by Stevens and Norrish,[84] evidence was obtained that a close connection exists between the Albert reversal and the "residual latent image," *i.e.*, the latent image surviving the chromic acid treatment. Stevens [85] followed this work with extensive experiments to test the relationship between the Albert reversal and the residual latent image, which he considers consists of sub-surface nuclei formed within the photographic grain and, therefore, not subject to destruction by the chromic acid treatment (Chapter IV, p. 168). The treatment with chromic acid leaves the internal nuclei to act as coagulation centers for the photo-product formed during the second exposure. Stevens states,

> "if the internal latent image of an exposed grain, which has been treated with acid dichromate solution, has this effect, it will prevent, or at least hinder, the formation of new surface nuclei and the grain will be desensitized. It therefore follows, necessarily, that the behavior of the reversal will be exactly similar to the behavior of the latent image."

Stevens found that both the Albert reversal and the residual latent image occur with acid dichromate (potassium dichromate 2 gms., sulfuric acid 10 cc., distilled water 1000 cc.) treatment *following* the first exposure. Both can be removed by sufficiently prolonging this treatment or using full strength acid permanganate. However, with weaker solutions, both effects are made to appear. Strong solutions of acid permanganate seem to attack the internal as well as the external nuclei.

It was found that both the residual latent image and the Albert reversal can be produced in emulsions treated with acid dichromate solution for twenty-four hours prior to the first exposure. This treatment, according to Stevens, removes all surface nuclei, and he claims that this experiment demonstrates that the Albert effect is independent of the surface nuclei. The fact, however, that his treated emulsion retained some sensitivity makes it appear doubtful that all the surface nuclei had been destroyed.

To demonstrate that the residual latent image consists of internal nuclei, Stevens carried out experiments in which a ten per cent solution of sodium sulfite was used on the grains after the first exposure and chromic acid treatment. Ferrous oxalate developer was used because it has no solvent action and, therefore, does not develop grains if the surface nuclei have been removed.[83] After treatment with sodium sulfite to dissolve the surface of the silver bromide grain, the ferrous oxalate developer was found to develop the image corresponding to the original exposure.

Stevens showed further that the residual latent image and the Albert reversal exhibit similar reciprocity law failure. He says,

> "it may, in fact, be claimed that every characteristic of the behavior of the residual latent image is accompanied by an exactly similar characteristic in the behavior of the Albert reversal. This can be regarded as an experimental proof showing that the residual latent image is the origin of the desensitization which gives rise to the Albert reversal."

It seems clear from Stevens' work and that of Lüppo-Cramer that the nuclei formed in the interior of the grain by the first exposure play a part in the desensitizing action observed in the Albert effect. This effect is greatest in the grains which have least of the original sensitivity centers left at the surface. Since exposure converts the sensitivity centers into the more easily oxidized latent image, the action of the oxidizing bath is increasingly effective with increasing exposure. Thus, grains with a higher pre-exposure have a greater tendency in the second exposure to produce the latent image in the interior rather than at the surface. This explains the reversal obtained.

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PART III

DEVELOPMENT AND THE AFTER PROCESSES

CHAPTER VIII

THE MECHANISM OF DEVELOPMENT

The photographic process depends upon the fact that the reaction $Ag^+ + e \rightarrow Ag$, *i.e.*, the reduction of silver ion to metallic silver by a developing solution, proceeds much more easily for an exposed silver halide grain than for an unexposed grain. The change which light produces in the grains to make them developable is the subject of Chapter IV. The present chapter discusses the mechanisms which start the reduction of an exposed grain and continue it once it has begun. It is necessary to distinguish between two kinds of development, generally known as *physical* and *chemical* development.

Typically, a *physical* developer contains a reducing agent, such as the benzenoid compounds generally used in developers, free silver ions, and a weak acid, such as acetic or citric acid. These solutions deposit silver upon suitable nuclei, such as those formed in the silver halide grains by light. In a true physical developer, therefore, the silver which forms the image is not derived from the silver halide of the emulsion. On the other hand, in *chemical* development, the silver bromide grain itself is reduced, starting from specific points of the surface. The developer does not contain any free silver ions and has a much lower oxidation-reduction potential, *i.e.*, it is a stronger reducer, than the acid solutions referred to above.

Much light has been thrown upon the process of development by the pictures showing the structure of the developed silver obtained by means of the electron microscope.* These pictures show very clearly the difference in structure between images produced by physical and by chemical development. The silver deposited from a physical developer is in the form of a fluffy mass composed apparently of very small particles of silver, while that produced by chemical development consists of definite filamentary strands resembling somewhat a mass of seaweed. In ordinary developing practice, both types of development may occur, since the solutions contain substances which dissolve silver bromide, the commonest of which is sodium sulfite. Interesting photomicrographic evidence of such competition in the case of a *p*-phenylenediamine developer is presented by Frieser.[1] For such solutions, the reduction of the silver is initiated by chemical development, but physical development occurs in the later stages.

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* The microscopy of the developed grain and the application of the electron microscope to its problems are discussed in Chapter XXI, p. 834.

Physical development is somewhat less complex than chemical development and is therefore discussed first, although from a practical viewpoint it is less important than chemical development.

PHYSICAL DEVELOPMENT

Bullock [2] measured the exposure required to produce an image for physical development compared with that necessary for chemical development and found that, for physical development, the exposure is approximately five times greater than for chemical development. The factor was determined for a fine-grain emulsion (Slow Lantern plates); there is reason to believe that for faster emulsions, the factor is considerably greater, but the matter is complicated by the very heavy deposition of fog if development is prolonged beyond the minimum time to produce an image. It appears possible that the latent image for physical development differs somewhat in its nature from the latent image for chemical development.

Two types of purely physical development are known. If solutions which can deposit silver are allowed to act on an exposed photographic material in the presence of the silver halide of the emulsion, the process is known as *pre-fixation physical development;* but if the silver halide is first removed by a solvent, such as thiosulfate, the process is known as *post-fixation physical development.* In both cases, the developing solution is of the same nature and the reaction is probably identical. The differences between pre-fixation and post-fixation images are fully explicable on the assumption that not all the silver nuclei are on the surface of the grain and, therefore, not so available before fixation as afterward. The final image produced by physical development is characteristically composed of very fine particles and is easily dissolved, so that the image after pre-fixation development must be fixed with care.

For post-fixation development, the solvent for the silver halide and the manner of its use are of importance. The very finely divided silver image on which the silver is to be deposited from solution is very reactive because of the small size of its particles, and it is easily oxidized and dissolved by aerated solutions of the fixing agent. The greater the complex-forming action of the solvent, the greater this effect becomes. Prolonged treatment with acid thiosulfate removes all traces of the latent image, as would be expected from the known solubility of silver in such baths.[3] This effect increases with time, temperature, acidity, and agitation. However, even alkaline hypo, which has little effect on a developed silver image, seriously affects the latent image for physical development, especially if the solution has been aerated. Perhaps the least effect is produced by sodium sulfite as the solvent. Unfortunately, it cannot be used with emulsions containing a high concentration of iodide; in this case, no solvent is suitable for quantitative work. A residual image may be obtained by the use of concentrated alkaline hypo or concentrated potassium iodide.

The influence of the number and size of silver nuclei in physical development was investigated by Arens and Eggert [4] and by Arens.[5] Proceeding from experiments with silver sols of known particle size and concentration, they showed that the mass of silver precipitated from a silver-ion solution by a physical developer (*p*-phenylenediamine sulfite) is independent of the size of the particles and proportional to their number. This rule likewise applies to gold particles. It is valid, however, only within certain limits. For very high concentrations of nuclei, the growth is less than proportional to their number; the relative rate of growth also decreases for particles larger than 10^{-15} grams, although the absolute rate of growth is still increasing. Both phenomena were explained as resulting from local exhaustion of the developing solution.

As has been stated, a physical developer is one which contains free silver ions and a reducing agent. For a practical physical developer, the solution must be stabilized by the addition of a weak acid or a compound which forms a complex with the silver ion, *e.g.*, sulfite. In this way, the solution is relatively stable and yet will readily deposit metallic silver upon suitable nuclei. In time, however, such a solution will plate out most of the silver on the container or any material immersed in it. Frequently, heavy fog is caused by the general deposition of silver on the surface of the gelatin, but this can be wiped off the wet emulsion or, in extreme cases, removed by an oxidizing agent without the image being seriously affected, since the image is formed inside the gelatin and is thus protected to some extent by it.

The oxidation-reduction potentials involved indicate the conditions necessary for the stability of the solution, and the electrochemical aspects of physical development are discussed in more detail in Chapter XII, which deals with the redox potentials of developers. When a silver salt solution is added to a reducing solution, there is an adjustment of the oxidation potentials of each to a common value intermediate between the two. This takes place by oxidation of part of the developing agent and a corresponding reduction of silver ions. If the potentials are initially very different, a large amount of the latter is reduced to silver. In the case of silver nitrate, if metol is used as the reducer, nearly all the silver may be thrown out of solution. If, on the other hand, silver sulfite in the presence of excess sulfite is added to an acid metol solution, very little silver is precipitated.

In explanation of the selectivity of deposition, two theories have been advanced. According to one, the silver specks of the latent image serve as crystallization nuclei for silver present in the developer as a supersaturated solution. According to the other theory, the silver specks also act as catalysts for the reduction of the silver ion.

Silver-bearing solutions of the type used for physical development are capable of maintaining a relatively high degree of supersaturation in dissolved silver over considerable periods. This supersaturation is decreased by the presence of surfaces onto which the metallic silver may plate out. Volmer[6] believes that a supersaturation of the order of a million times that of the normal solubility might occur. It is therefore understandable that if silver nuclei are present, the silver from the solution deposits upon them and the latent image is thus developed.

However, physical development is controlled by kinetic phenomena as well as by the thermodynamic conditions just discussed. The addition of acid to the developer not only lowers the silver potential, but diminishes the rate of reduction. An acid-containing developer, therefore, furnishes the reduced silver at a lower rate than one containing more hydroxyl ions. The rate of reduction of the acid-containing developer is adjusted better to the rate of crystallization on the silver nuclei, and spontaneous plating out is therefore lessened.

Sheppard and Mees [7] and James [8] showed that the reduction of silver ions by various developing agents is strongly catalyzed by metallic silver, and, according to James, the catalytic action of silver nuclei upon the reduction of silver ion is caused by the adsorption of silver ion at the surface of the metallic silver. Volmer [6] showed that the reaction of developing agents with atmospheric oxygen is likewise accelerated by the presence of colloidal silver, and possibly, therefore, the developing agent itself is activated as a reducer by the presence of the colloidal metal. These investigations support the theory, first advanced by Volmer, that the latent image has a catalytic effect on the reduction process proper as well as on the deposition of the silver. In either case, development obviously continues by the mechanism by which it was initiated.

CHEMICAL DEVELOPMENT

In its ideal form, the solution used in chemical development contains no free silver ions or silver solvent. This pure type is most closely approached by the ferro-oxalate developer, which contains no sulfite or other silver solvent and in which the solubility of silver bromide is very low indeed. Most of the other practical developers contain silver solvents, such as sulfite, but, even then, development is probably due in large part to the reaction of the developing agent with the silver halide grain itself.

Several theories have been evolved as to the mechanism of chemical development, and various types of experiments have been carried out to test them. It is probable that certain of the mechanisms suggested do not exclude, but supplement, each other, and this may explain some of the complexity of the literature. There are hypotheses relating to the initiation of development which apply directly only to the organic developers, such as hydroquinone. Thus, all the work on adsorption of developing agents and the influence of their oxidation products has been carried out on only those developing agents, and the properties of ferro-oxalate have largely been ignored. In view of the greater simplicity of the chemical reactions of ferro-oxalate, the complete reversibility of its reaction, and its freedom from solvents for silver halide, it would seem to have advantages as *the* typical developer. This view was adopted by Sheppard and Mees in their early work on the theory of the photographic process.

For many years, the most generally accepted theory of the mechanism of development was the so-called *supersaturation theory*. This was proposed first by Ostwald [9] and, in a somewhat modified form, by Abegg [10] and Schaum.[11] Sheppard and Mees [7] considered it in entire consonance with their experimental results. It assumes that the deposition of silver takes place from a supersaturated solution and that chemical development is closely related to physical development. According to Ostwald, the silver halide dissolves in the developer, which has penetrated to the grain surface. Then the silver cations are reduced by the developing agent in a thin layer around the grain. The silver atoms thus formed are in solution, and the reaction is supposed to stop unless silver is present in the solid form, on which that from the solution can precipitate. It is assumed that in an exposed grain, the latent image furnishes the silver nuclei for the beginning of precipitation of the silver from the developer solution. Once started, the process continues until the entire grain has been reduced to metallic silver. According to the Ostwald theory, the silver nuclei facilitate the deposition of the reduced silver but not the reduction itself. On the other hand, the reducing action of a reversible developer slows down with rising concentrations of silver atoms in the solution and, at high supersaturations, approaches a standstill. If silver nuclei break the supersaturation, the reduction will continue, and in this sense the action of the silver nuclei might be called catalytic.

The Ostwald theory allows a rather simple treatment of certain problems connected with development, and it has been widely used. There are many objections, however, to this theory. The production of a high concentration of reduced silver in solution should stop the reduction process only if the latter is a reversible reaction, and it is therefore difficult, on the basis of the Ostwald theory, to understand the action of the irreversible organic developers containing sulfite. Staude,[12] in a review of the literature, like many other authors (see below) stresses the importance of true catalysis and adsorption for the initiation and the mechanism of development and points out that a large number of phenomena common to heterogeneous catalytic reactions appear also in development. Thus, the Ostwald theory should not be considered an adequate representation of the mechanism of development. However, for problems which are not concerned with the actual mechanism of the process but only with the equilibria which are finally attained, i.e., the thermodynamic considerations, the ideas of Ostwald are still of real value.

Direct evidence against the Ostwald theory is furnished by observations with the electron microscope. These reveal an unmistakable difference in the nature of the silver deposits obtained in physical and in chemical development. The mechanism of physical development described above is not contradicted by the electron micrographs of the silver. However, it is difficult to visualize how a mass resembling seaweed (Figure 97), which is formed in chemical development, could originate in a process having the mechanism suggested by Ostwald. That the filaments are not formed in the interior of the crystal grains but by extrusion from them is shown in the series of pictures illustrating progressive stages of development of small emulsion grains (Figure 99). At first, a few filaments are extruded, and these increase in number and length as development is continued until, finally, the silver bromide grains are replaced by the filamentary silver. In the development of very small grains, such as those of Lippmann emulsions, each individual grain appears to be converted into a single filament of silver (Figure 98).

The filamentary silver produced in development closely resembles the "hair" silver described by various authors and investigated by Kohlschütter.[13] It is likely that both originate in similar processes. According to Kohlschütter, hair silver is formed by the reduction of silver sulfide with hydrogen at 444° C. The formation depends upon several factors, *viz.*, reduction rate, mobility of the silver ions in the crystal, and

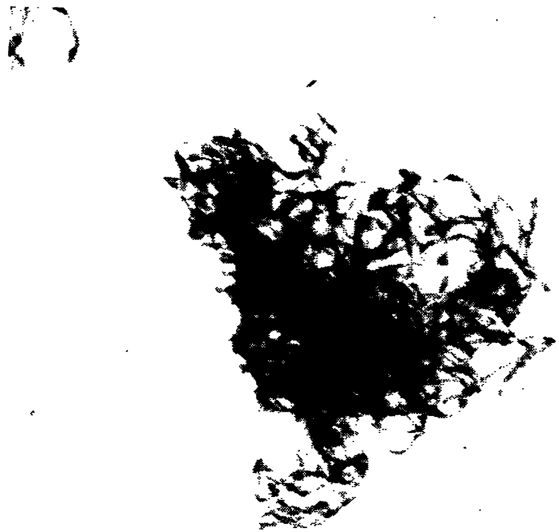

FIG. 97. Silver grain produced by development with amidol. ×40,000.

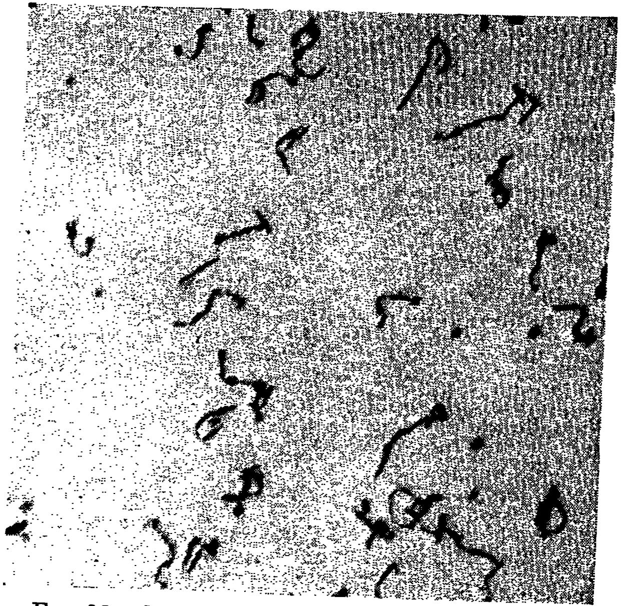

FIG. 98. Lippmann emulsion grains after development. ×50,000. (For the grains before development, see Figure 14, p. 34.)

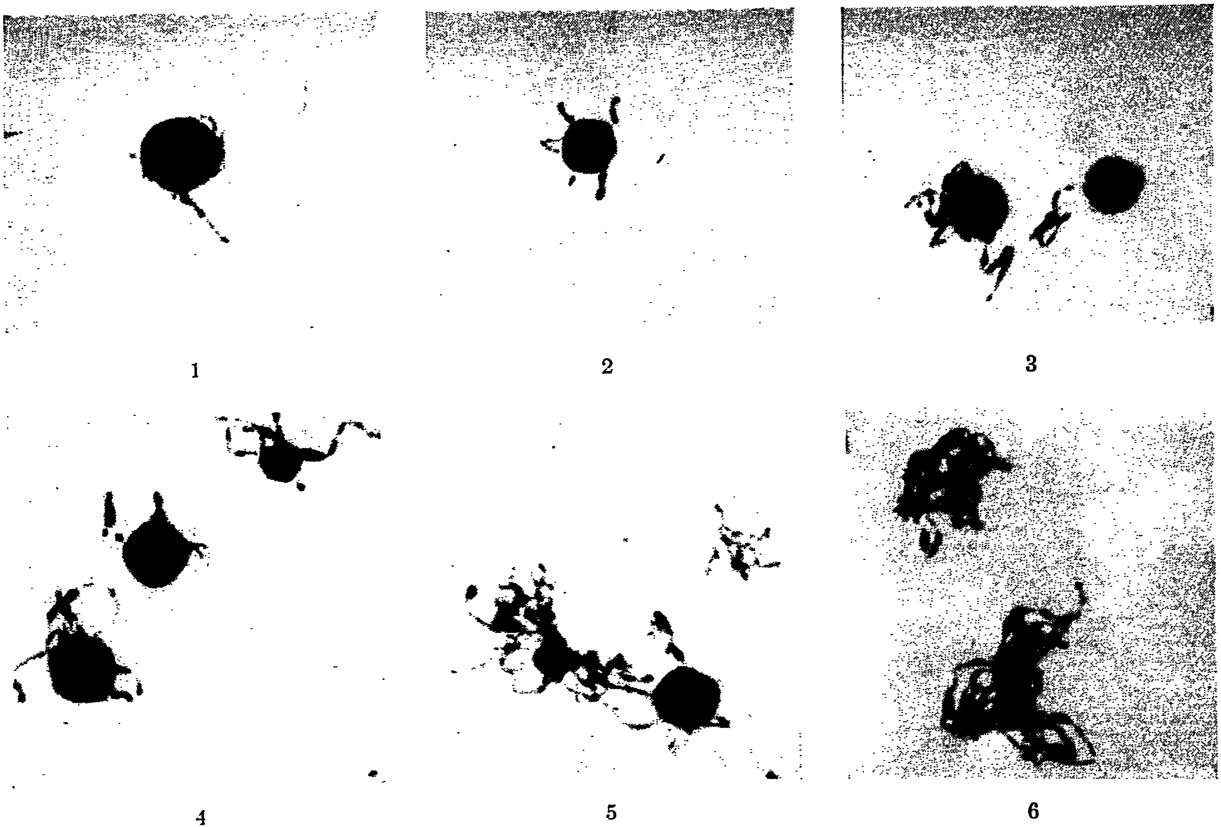

FIG. 99. Stages in the development of silver bromide grains. ×50,000.

catalysis by nucleus formation; the reaction is initiated by a silver speck and continues at the interface of silver and sulfide. When the silver ion is neutralized, it is released from the electrostatic forces of the lattice and has a high energy content owing to the heat of reaction. Both factors make the silver atom leave the surface of the sulfide crystal, pushing ahead the silver already present. The growth of a silver hair continues as long as the silver ions at the place of reaction are restored by migration in the crystal. The mobility of the ions in silver sulfide at the temperature of reduction is obviously high enough to provide for a sufficient supply. The only other compound which, in Kohlschütter's experiments, formed hair silver was silver halide. Silver chloride produced small threads of silver if reduced at a temperature of 550° C. Although such a high temperature is unlikely to be reached in development, it should be kept in mind that the reduction of silver ion by hydroquinone may easily have a heat of reaction of about 10,000 calories and that this may produce hot points in the reducing crystal. Further, the growth of microscopically visible hair silver observed by Kohlschütter at a magnification of 130 diameters requires migration over much greater distances than the formation of the fine deposits illustrated in Figure 97.

The structure of the silver deposits formed in chemical development and revealed by the electron microscope shows that the reduction is localized in spots and proceeds at the silver, silver halide interface. Rabinovich and Shteifon [14] carried out a photomicrographic study of the development of large, flat individual silver bromide grains. Under the conditions employed, development spread on the grain in circular zones, starting from invisible nuclei, and formed a well-marked interface between the reduced silver and the silver halide. The rate of increase of the developed area was proportional to the extent of the silver, silver halide interface.

The phenomenon of reaction at an interface is not a rare one. The reduction of cupric oxide by hydrogen is markedly accelerated by the presence of copper nuclei. The thermal decomposition of many crystalline compounds, among them silver oxide, silver oxalate, and silver permanganate, commences at nuclei and proceeds at the interface of the crystal and the solid reaction product. The interface is evidently a region of enhanced reactivity, even in reactions which proceed without the participation of external materials.

An adsorption theory of chemical development was suggested by Bancroft:[15]

> "If the reducing agent is adsorbed much more strongly by exposed silver bromide than by unexposed silver bromide, the former will develop more rapidly than the latter, and we shall get a negative. If the reducing agent is adsorbed more strongly to unexposed than to exposed silver bromide, we shall get a positive. If there is not much difference in the adsorptions, we shall have exposed and unexposed silver bromide developing at so nearly the same rate that we get a more or less uniform fogging."

This suggestion was developed in various ways, and the study of the induction period in photographic development was particularly helpful in these investigations.

When an exposed plate is immersed in a developer, in some cases traces of the image become visible almost immediately, while in other cases a certain time elapses before an effect of development can be seen. This time lag is called the *induction period;* its immediate importance for the study of the initiation of development is obvious. Lainer[16] found that small concentrations of soluble iodide in the developer diminish the induction period, and Lüppo-Cramer[17] showed that the same effect occurs from the addition of small quantities of certain basic dyes and of the colored oxidation products of many developers, such as amidol, metol, and so forth. The Lainer effect was attributed by Lüppo-Cramer to the partial disintegration of the silver bromide grain by the local conversion of the bromide into iodide (Chapter VII, p. 271). In this way, the silver nuclei produced by exposure are supposed to become more effective in accelerating reduction. This hypothesis of the unpeeling of the nuclei (Keimblosslegung) has often been reaffirmed by Lüppo-Cramer, while Sheppard and Meyer[18] consider it "artificial and forced." These authors measured the influence which the treatment of the exposed film with potassium iodide solutions has on the Watkins factor.

The Watkins factor (Chapter XI) is the quotient of the time of development necessary to produce a given density divided by the time at which the first traces of the image appear.[19] Sheppard and Meyer found that the Watkins factors of metol developers are not influenced by treatment of the sensitized material with the iodide solution. Such treatment, however, doubles the factor for a glycin developer and increases it for a hydroquinone developer to as much as six times its original value. These differences between the developers are not readily explained by "Keimblosslegung," and Sheppard and Meyer give the following explanation: With a metol developer, the image appears very quickly, while a hydroquinone developer has a considerable induction period. If the sensitized material is treated with iodide solution before development, this period of latency will become smaller and the Watkins factor will increase correspondingly. The induction period itself is supposed to depend upon the time which the developing agent requires to become adsorbed to the silver halide grain. This adsorption of the developing agent, according to Sheppard and Meyer, takes place by virtue of a chemical complex of the developing agent and the silver halide, and compounds which promote this complex-formation reduce the induction period.

Treatment of silver bromide crystals with potassium iodide converts the surface of the crystals, at least partially, to silver iodide. If this silver iodide has a greater tendency to form complexes with the developing agent, the iodide-treated grains will adsorb the developing agent more readily than does the untreated silver bromide, the induction period of development will decrease, and the Watkins factor will increase. The authors substantiated the fact that the tendency of silver bromide to adsorb compounds increases in the presence of potassium iodide by showing that the adsorption of the dye safranine to silver bromide is considerably facilitated if potassium iodide is present in the solution from which the adsorption takes place.

Sheppard and Meyer suggest, on the basis of their experiments, that development proceeds as follows: The developing agent, after penetrating the gelatin, forms complexes with the silver halide at the surface of the silver halide grains. These complexes, in the presence of silver nuclei, break down with the formation of metallic silver and the oxidized developing agent. The metallic silver for the initiation of this process is provided by the photolytically formed silver of the latent image. After the reduction of the grain starts, it proceeds autocatalytically because of the silver formed. This is in agreement with the suggestion which Piper [20] made as early as 1908 that "we may look upon development as being an action of a catalytic nature, the latent image being the catalyzer." The importance of a suitable nucleus, according to Sheppard,[21] is twofold. Its interface with the silver halide provides the necessary ionic deformation for reactivity, and, on the other hand, it provides a break in the adsorption layer (Chapter VIII, p. 319), a starting-point for displacement processes.

A direct experimental investigation of the adsorption of the developing agent to silver halide under developing conditions has not been possible because of the difficulty of separating adsorption from reduction. Wulff and Seidl [22] attacked the problem by substituting for the organic reducer a meta-substituted compound of otherwise similar type which does not develop, *viz.*, resorcinol (*m*-dihydroxybenzene) for hydroquinone. Their experiments indicated that in alkaline solution this substance is adsorbed to silver bromide. Apart from certain inadequate controls (pH stabilization), it is difficult to appraise the significance of these results for the adsorption hypothesis because resorcinol is not a developer.

The effect of dyes and of oxidation products on the induction period was investigated sensitometrically by Luther and Frötschner.[23] The addition of as little as 0.008 gram per liter of oxidized amidol to a hydroquinone developer produced the effect. In the absence of sulfite, a hydroquinone developer had only a short induction period, obviously because the oxidation products were not removed by sulfite, while the induction period greatly increased if the hydroquinone was protected from aerial oxidation. The addition of bromide to such an air-free developer produced a much greater depression of development than in the presence of air, and Frötschner considers it questionable whether hydroquinone free from oxidation products would act as a developer in the complete absence of air. The oxidation products cut down the induction period even if they are used in a predevelopment bath and the emulsion is thoroughly washed afterward. From this, it was concluded that the effect depends upon adsorption of the additions to either the halide or the latent image.

This work was continued by Staude[12,24] and extended to cover practical developers containing sulfite. A hydroquinone developer so prepared that it was free from oxidation products showed a prolongation of the time of appearance in the presence and the absence of the usual additions (sulfite, potassium bromide). With metol, the time of appearance in strongly alkaline solutions was so short that only a weakly alkaline solution could be studied, and with amidol a marked effect of the oxidation products was evident only at pH values below 6.0. Staude found that the time of appearance of fog, that is, the development of unexposed silver bromide, was not prolonged by the absence of oxidation products; and he concluded that initiation by oxidation products is not necessary for the development of fog but that the latter is produced by the developing agent itself.

Staude assumes that the latent image consists of electron concentrations at the sensitivity specks of the silver halide crystals and that the oxidation products are adsorbed to the exposed grains by virtue of their affinity for these electrons. A reducing agent which forms addition compounds with its primary oxidation products is then preferentially adsorbed to the exposed grains through the mediation of the oxidation products. When reduction begins, more oxidation product is formed, and the reduction continues as an autocatalytic process. Development of solarized grains is retarded because, instead of electron concentrations, nuclei of metallic silver are present to which the oxidation products are not adsorbed. Once development of the solarized grains has begun, it proceeds normally, oxidation products being formed which catalyze the reduction. According to Staude, the capacity to form addition compounds with its oxidation products is characteristic of a developing agent. The explanation given by James and Weissberger for the catalytic action of the oxidation products in the autoxidation of various developing agents has some bearing on this subject (Chapter X, p. 381). However, it is difficult to understand how Staude's theory can deal with the simple irreversible inorganic developers and organic developers such as durohydroquinone, which are not known to form addition products with their oxidation products, unless Staude is correct in suggesting that the addition products are formed by the compounds when adsorbed, even if they are otherwise unknown. The inhibiting effect of oxidation products on developing agents like *p*-phenylenediamine presents another objection to Staude's theory, while the instability of concentrations of electrons at concentration specks has already been discussed (Chapter VI, p. 244).

The adsorption of the developing agent to the silver halide was studied from a different point of view by Schwarz and Urbach [25] in their *surface charge theory*. These authors, instead of asking how a developer reduces the exposed grains, investigated the problem of why the unexposed grains are not reduced and what it is that protects them from reduction. The protection is not always present. Silver bromide, for instance, which is precipitated in the presence of an excess of silver nitrate or in the absence of gelatin is readily reduced in a common developer without exposure to light. Schwarz and Urbach carried out experiments on the stability, coagulation, exposure, and developability of halogen silver sols prepared with or without excess of bromide and with or without gelatin. On the basis of these experiments, they suggested that the protection of unexposed silver halide from development is due to a negatively charged layer which surrounds the silver halide grain formed in the presence of excess of bromide (Chapter III, p. 90) and that the gelatin protects this charged layer. The grains are not reduced by the developer, because the protective charged layer keeps the developer ions away from the grain. Exposure to light removes an electron from one of the surface bromide ions to the interior of the grain, where it is caught by a silver ion. The latent image, *i.e.*, the effect of the exposure upon development, is not associated with the silver atom formed but with the gap in the charged layer caused by the absence of this electron. This gap in the charged layer is thought to allow developer ions to reach the grain and so reduce it.

The surface charge theory was accepted in its essential features by Evans and Hanson.[26] These authors point out that the excess halide which forms the negative charge may be considered either as simply adsorbed to the crystal surface or as part of the crystal lattice. It may be assumed that the latter type plays an imporof the hydroquinone originally added was present in the filtrate. The difference of 17.5 per cent was called "adsorbed," no attention being given to the fact that if a loss occurred before ultrafiltration, it could very likely occur during ultrafiltration, which is a time-consuming operation. This obviously happened, because when Perry, Ballard, and Sheppard [31] repeated Rabinovich's experiments under more stringent conditions, *e.g.*, careful protection of the solutions from aerial oxidation, no conclusive evidence for an adsorption of hydroquinone to colloidal silver was found. According to these experiments, only a very slight adsorption, if any, takes place.

Volmer [32] described the catalytic action of colloidal silver on the reaction of developing agents with atmospheric oxygen. This is, in many respects, similar to the reduction of silver halide (Chapter X, p. 377). Its rate increases when colloidal silver is added to the solutions, as shown by their more rapid discoloration. On the basis of these results, Volmer originated the theory that photolytically formed silver accelerates the reduction of silver halide and initiates development, which then continues by the same mechanism.

James [33] introduced silver nuclei into silver chloride grains which were prepared in the presence of gelatin and compared their reduction with that of grains without silver nuclei, using hydroxylamine as the developing agent. The reaction was followed by measuring the evolution of nitrogen (Chapter X, p. 376). Figure 100 illustrates some typical results. Both samples were reduced by the hydroxylamine, but the nucleated sample was reduced at a much greater rate than the pure silver chloride. In analogy to actual development of a photographic emulsion, curve 2 represents image development, and curve 1, fog formation. This serves to emphasize that development is essentially a kinetic phenomenon. Except under very restricted conditions, both exposed and unexposed grains of the photographic emulsion are attacked by the developing agent. The distinction between them lies in the fact that the exposed grains are reduced at a substantially greater rate than the unexposed ones. Other experiments were carried out by the same author on the catalytic action of colloidal silver in the reduction of silver ions in solutions of hydroquinone.[8,34] It was shown that in these cases the catalytic action depends upon adsorption of silver ions to the silver, and a corresponding mechanism was suggested to explain the greater reactivity of the nucleated silver chloride grains.[35]

Erbacher[36] had shown that the radius of silver ions is increased by adsorption to silver, because the metal electron attracted by the ion weakens the nuclear field of the latter. A similar deformation, modified by the crystal forces, is to be expected in the case of a silver bromide particle containing a silver nucleus such as that produced by light action or partial reduction by a developing agent. According to James,[35b] this deformation may be the basis for the enhanced reactivity toward certain reducing agents; namely, the developing agents, which require an appreciable energy of activation. If, however, the activation energy of the reaction between a reducing agent and silver ions is very small or zero, the deformation of the latter at the silver surface cannot increase the reaction rate significantly, and no appreciable silver catalysis can arise.

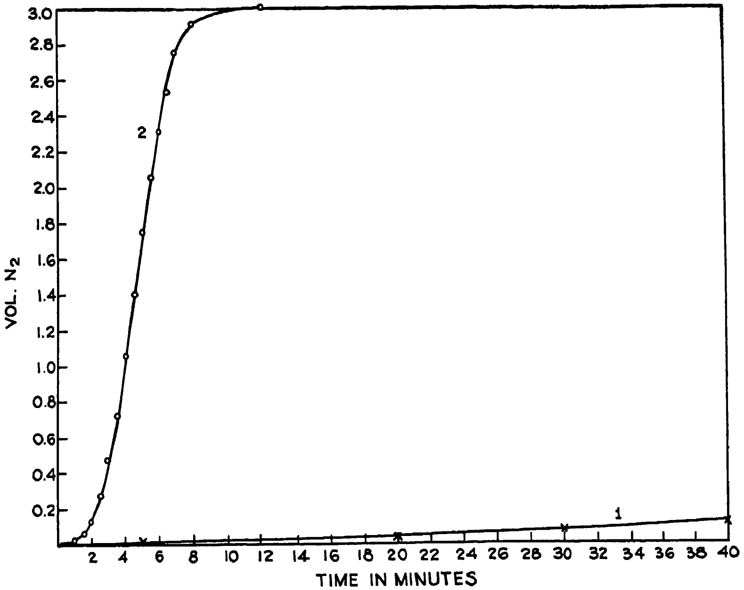

FIG. 100. Evolution of nitrogen from silver chloride developed with hydroxylamine (1) without and (2) with the addition of silver nuclei.

An electrochemical explanation for the participation of photolytically formed silver in the initiation of development is given by the silver electrode theory of Gurney and Mott.[37] These authors offer a tentative theory for the mechanism of photographic development in connection with their theory of the formation of the latent image. They postulate that development of the grain is produced in much the same manner as formation of the latent image by light exposure. They assume that the latent image consists of a clump of silver atoms on the surface of the grains. The mechanism by which they suppose development to take place can be described as follows:

The energy level of the electrons in the adsorbed ion of the developing agent lies above the highest occupied level of the metal and, therefore, when the ion comes into contact with the silver speck of the latent image, it releases an electron to the silver. Any metallic silver in contact with the developer therefore acquires a negative charge on the latent-image speck, and the charge then attracts further positive silver ions existent at interlattice positions in the crystal. The speck of silver grows by the same mechanism as in the formation of the original speck of silver comprising the latent image, in which case the electrons are supplied by light action. In this way, Gurney and Mott assume that the entire grain of silver bromide becomes converted to silver, the bromine presumably passing into the developer as ion to replace the negative charge released by the developer. This, however, presents a difficulty: Since it is assumed that the developer does not penetrate into the grain, the bromide ions from the interior of the grain would have to migrate through the silver halide lattice. The analogy to the latent-image formation does not include this point, since in that case the escape of bromine atoms can occur by the migration of electrons. No experimental evidence is available, however, for a migration of bromide ions through non-reacting zones of a silver bromide crystal. It is improbable, therefore, that the continuation of development depends upon the mechanism proposed unless it is accompanied by a disintegration of the grain which provides for the escape of the bromide ions.

J. H. Webb * has developed the idea of the silver-electrode mechanism in a rather concrete form, combining it with the surface charge theory. As a starting point, he uses the exposed

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* Private communication.

silver halide grain, which he represents, for instance, as a plate, as shown in Figure 101, in which the charged condition around the grain is represented schematically. The surface of the silver bromide grain itself has an excess of bromide ions, which give rise to a negatively charged surface. However, just outside this negative charge, a positive layer of potassium ions must be present to neutralize the negative charge. Without such a neutralizing layer of positive ions, it would be impossible for the surface of the silver bromide grain to be covered with negative bromide ions, since the amount of such a charge in so small a region would give rise to explosive forces. A double charge layer, consisting of negative bromine ions on the grain and positive potassium ions in the gelatin just outside, may be considered to exist around the surface of each silver bromide grain. Grains with such a double layer (in solution) would move under an electric field as negatively charged bodies, since the negatively charged grain would be forced in one direction by the field, and the surrounding movable positive-ion layer in the opposite direction; but since at any point in the liquid there would be positive ions to form the surrounding positive shell, the double charge layer would be maintained. That the surface charges on the particles and surrounding charge layers do neutralize each other in the manner outlined is proved by the fact that the colloidal suspension does not possess a net charge of either sign but is neutral as a whole.

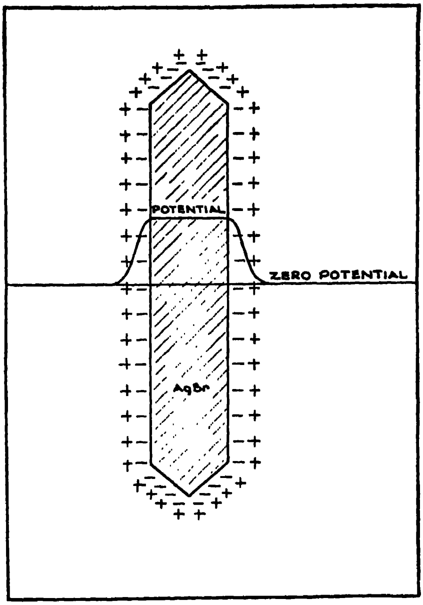

FIG. 101. Electrical condition surrounding a silver bromide grain.

It may be assumed that a grain, owing to its double charge layer, behaves toward outside charges and also those located inside the grain as a neutral body. An electron placed inside such a double charge layer would experience no force nor, in the same way, would an electron placed outside such a double layer. However, there is a marked difference in potential between the

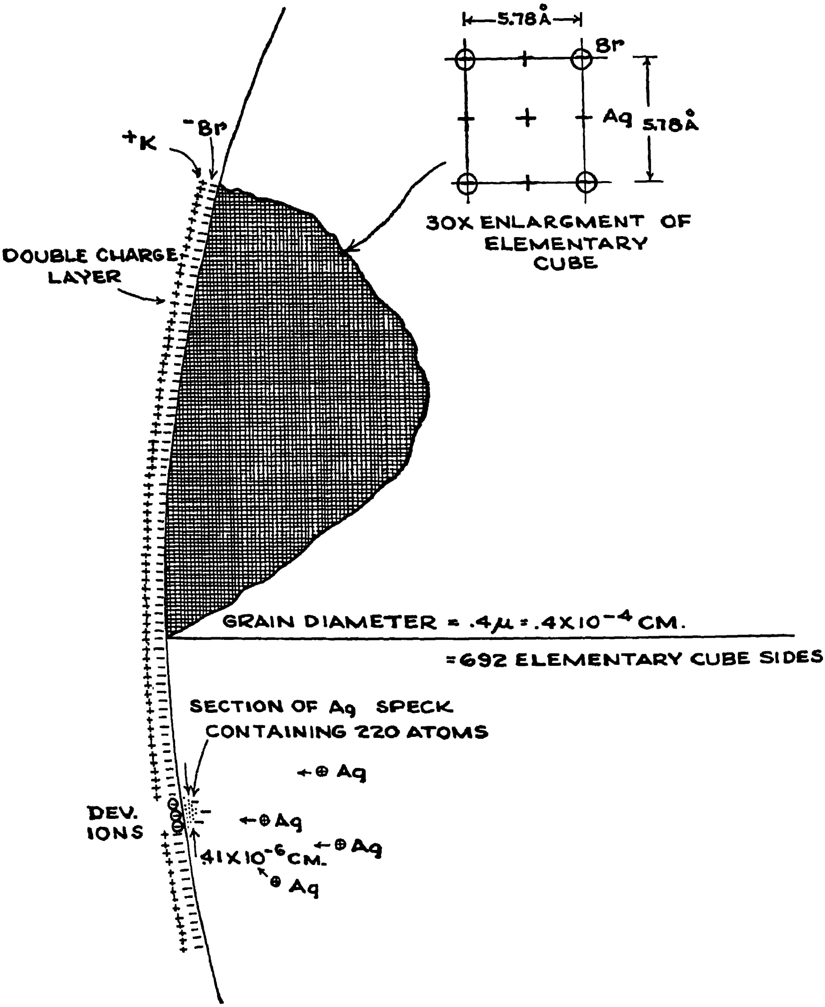
5.78Å
Br
Ag
5.78Å
30X ENLARGMENT OF ELEMENTARY CUBE
+K
-Br
DOUBLE CHARGE LAYER
GRAIN DIAMETER = .4μ = .4X10^{-4} CM.
=692 ELEMENTARY CUBE SIDES
SECTION OF Ag SPECK CONTAINING 220 ATOMS
⊕ Ag
DEV. IONS
⊕ Ag
.41X10^{-6} CM.
⊕ Ag
⊕ Ag

Fig. 102. Model of an exposed grain containing a latent image.

inside and outside of the grain, and the total jump in this potential occurs in the region between the two charge layers. The potential gradient between these charge layers accordingly gives rise to a strong electrical force between the layers, and an electron placed between them would experience a force toward the outside. It is considered that the double charge layer acts in this way as an effective potential barrier to the entrance of an electron into the silver bromide grain of the emulsion and prevents the developer from attacking the grain.

The conditions existing in the exposed grain containing a latent-image silver speck may be seen in Figure 102. This shows a greatly enlarged scale model of a charged grain surface with a clump of silver atoms on the surface which is supposed to represent the latent image produced by exposure to light. The clump shown includes 220 atoms, with approximately the correct spacing. This size was chosen as representing a fair mean of the values given by various workers.

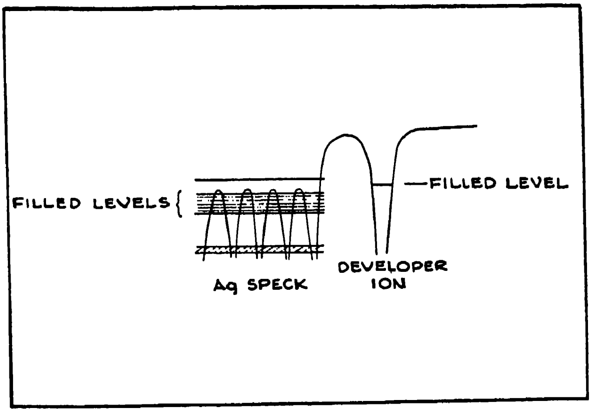

Fig. 103. Energy diagram of a developer ion adsorbed to a silver speck.

Webb assumes that development of a grain is initiated by the break in the double charge layer caused by the silver speck, permitting the negative developer ions to reach this silver speck. The latent-image speck is viewed as an electrode penetrating into the grain. The tendency on the part of the developer ions to release electrons to the silver causes electrons to pass to the electrode and charge it negatively. As explained by Gurney and Mott, this occurs if the electrons of the developer ions are situated in levels above the highest occupied energy levels of the silver metal, as illustrated in Figure 103. The penetration of this negative electrode into the silver bromide grain upsets the neutral electrical condition previously existing in the grain, and there arises an attractive force for the positively charged silver ions in the neighborhood of the latent-image speck. Some loose positive silver ions always exist in the crystal lattice owing to temperature motion, and these diffuse to the speck under the attraction of the negative charge there and enlarge the silver speck. Thus, it is supposed that the original silver speck of the latent image continues to grow by this mechanism. As this proceeds, the protective double layer is more and more ruptured, and a rapidly increasing area of the silver halide grain is exposed to the attack of the developer. The reduction of the grain therefore proceeds at an ever-increasing rate, and the grain is soon reduced throughout to metallic silver. Only in the initial stages of development is a silver bromide grain protected from a developer; and after the barrier is once penetrated, it is developable very rapidly.

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CHAPTER IX

THE DEVELOPING AGENTS

The factors which discriminate between exposed and unexposed grains in the development of the latent to a visible image and the mechanisms which have been suggested for this process are discussed in the preceding chapter. The present chapter deals with the chemical nature of the developing agents, *i.e.*, the reducing chemicals proper. However, the properties of developers, *i.e.*, developing solutions, depend not only on the developing agents but also on the hydrogen-ion concentration and ingredients such as sulfite and bromide. If, for instance, the oxidized and the reduced forms of a developing agent differ in their hydrogen content, a change in the pH will affect the activity of the developer. This is discussed from an electrochemical viewpoint in the chapter on the redox potentials of developing agents and developers. It presents a kinetic problem also, inasmuch as the molecules and the ions of the developing agent in question reduce the exposed silver halide at different rates. The pH of the developer may, furthermore, change the stability of the oxidation products of the developing agents as well as the potential barrier surrounding the silver halide grains and thus influence development. The specific conditions of the heterogeneous systems also control the effects of the oxidation products which may accelerate or retard development. The action of sulfite is manifold, inasmuch as it acts as a preservative for the developing agent (p. 382) and as a solvent for the silver halide.

In considering the relationship between chemical constitution and developing properties, it is necessary to remember that compounds may fail to develop either because they do not reduce the silver halide, regardless of exposure to light, or because they reduce the unexposed grains as well as the exposed ones. Whether a compound is a developing agent or not is judged by its action in a suitable solution on a normally exposed silver bromide or silver chloride gelatin emulsion. Compounds are disregarded which develop uncommon sensitive layers, such as iodide emulsions, but completely fog the common type of emulsions. Compounds which develop sensitive layers prepared with an excess of silver ions or without gelatin are also disregarded if they are not developers for ordinary emulsions. However, borderline cases of developing agents of theoretical interest are included here even though they are of no practical use.

Developing agents can be classified in two groups: those in which a metal undergoes a valency change and those which do not contain a metal with variable valency. The latter include the important organic developers and some inorganic ones, such as hydroxylamine and hydrosulfite. The first group contains purely inorganic substances, *e.g.*, ferrous fluoride, and metal salts of organic acids, such as ferrous oxalate and citrate.

DEVELOPING AGENTS CONTAINING METALS WITH VARIABLE VALENCY

A. and L. Lumière[1] reduced the solution of a pentavalent vanadium salt (vanadium pentoxide in acid) with zinc to the divalent state, filtered out the undissolved metal, and found that the solution developed. Tobin[2] found that the exhausted solution may be regenerated by treatment with zinc and suggested the system as a perpetual developer. Similar developers containing salts of chromium, tungsten, and molybdenum were reported by Liesegang.[3] All these developers are easily exhausted because of the antagonistic action of the oxidized metal ions. These diminish the reduction potential of the solution (Ch. XII) and oxidize metallic silver back to the ion, thus destroying the visible image and, in the case of fresh material immersed in a used developer, even the latent image. In ferrous sulfate, this state of exhaustion is reached at so low a concentration of ferric ions that ferrous sulfate alone does not act as a developer. However, Ammann-Brass[4] found that if he added metallic zinc or iron to a ferrous sulfate solution and thus continuously reduced the ferric ions to the ferrous state, he obtained a developer. The addition of the auxiliary reducing agent (metal) as a separate solid phase prevented its undesirable direct contact with the emulsion. The same effect should be obtained by electrolytic reduction or by reduction with hydrogen and a catalyst.

Another possibility for making the oxidized form of the developer innocuous lies in adding a substance which forms a complex with the ions of the higher oxidation state. This is obviously the mechanism by which ferrous salts become developers upon the addition of fluoride ions. The latter form with Fe^{+++} the complex ion FeF_6^{---}, while Fe^{++} does not form a stable complex with them.[5]

The developing agents mentioned are active in neutral or acid solutions. They contain the reducing agents proper as rather simple cations and show that a mechanism which discriminates between exposed and unexposed grains must also be effective with positive ions (See Chapter VIII). The idea that developers are substances capable of forming addition products with their next higher oxidation products is not supported by the type of developers discussed here; at least, no evidence is available at present that ferrous and ferric ions combine either in solution or when adsorbed.

The ammoniacal cuprous oxide solution of Carey Lea [6] may be mentioned as a purely inorganic metal-containing developer which works in alkaline solutions. The alkalinity of this solution is so high that it absorbs carbon dioxide from the air, which is avoided in the ammoniacal cuprous chloride, bromide, or iodide solutions described by A. and L. Lumière.[7] However, for the reasons mentioned above, these developers, too, produce only weak images.

A metal-containing developer which has had great practical importance is the ferrous oxalate developer discovered by Carey Lea [8] and used in their investigations by Hurter and Driffield and Sheppard and Mees.[9,10] It is made by adding ferrous sulfate solution to an excess of potassium oxalate solution, the whole being slightly acid. The iron in this solution is present as a complex anion, $Fe(C_2O_4)_2^{--}$, which is stable in the presence of excess free oxalate ions, according to the equilibrium

$$Fe(C_2O_4)_2^{--} \rightleftharpoons FeC_2O_4 + C_2O_4^{--}. \qquad (1)$$

When the ferro-oxalate is present in solid form, the constant for the above equilibrium is 0.37 at 20° C.

In its simplest terms, development by ferro-oxalate may be formulated as follows:

$$\mathrm{Ag^+ + Fe(C_2O_4)_2^{--} \rightleftharpoons Ag\ (met.) + Fe(C_2O_4)_2^-}. \qquad (2)$$

According to spectrophotometric data, it may be assumed that in the presence of excess oxalate, all the iron is present as complex ion, and the ferric complex becomes $\mathrm{Fe(C_2O_4)_3^{---}}$. However, the adjustment

$$\mathrm{Fe(C_2O_4)_2^- + C_2O_4^{--} \rightleftharpoons Fe(C_2O_4)_3^{---}},$$

according to Sheppard and Mees, does not affect the main reaction; therefore, for convenience, the symbols $\mathrm{Fe^{--}}$ and $\mathrm{Fe^-}$ are used for the ferrous and ferric complexes.

Sheppard and Mees determined, in the presence of bromide ions, the ratio of $\mathrm{Fe^{--}}$ to $\mathrm{Fe^-}$ above which the solutions are reducers and below which they are oxidizers. Test strips were made by exposing areas of plates in a sensitometer. In the reaction mixture, development either took place or was inhibited. If the limits were narrowed on either side, upper and lower values for the ratio were obtained. The reverse balancing method, in which equilibrium is attained from the opposite side, consists in determining the concentrations which just bleach or fail to bleach the silver of a negative. The following table shows the results obtained by this method:

TABLE XV

Volume in cc.	*No. of gram-mols. ferrous iron*	*Gram-mols. ferric iron*	*Gram-mols. of bromide*	K	+ = *developer* − = *oxidizer*
25	0.000092	0.00321	0.00101	710	+
25	.000092	.00350	.00101	650	−
25	.000092	.00374	.00101	600	−
		Value lies between 710 and 650.			
25	0.000046	0.00160	0.00101	710	+
25	.000046	.00165	.00101	690	−
		Value lies between 710 and 690.			
25	0.000036	0.00180	0.00101	650	−
25	.000036	.00130	.00101	690	+
		Value lies between 690 and 650.			

The experiments show that for 25 cc. in $N/25$ bromide, the concentration of ferric ion must be thirty-six times that of the ferrous for the system to be in equilibrium. The last column gives values for an equilibrium constant K, which was derived as follows:

The concentration of the silver ions in solution is determined by that of the free halide ion. For silver bromide,

$$\mathrm{Ag}^{+} + \mathrm{Br}^{-} \rightleftharpoons \mathrm{AgBr}\ (\text{solid}). \tag{3}$$

From equation 3 it follows that

$$\frac{[\mathrm{Ag}^{+}][\mathrm{Fe}^{--}]}{[\mathrm{Fe}^{-}]} = \text{constant},$$

the concentration of metallic silver in the presence of solid silver being constant. Since, from (3),

$$[\mathrm{Ag}^{+}][\mathrm{Br}^{-}] = \text{constant},$$

$$\frac{[\mathrm{Fe}^{--}]}{[\mathrm{Fe}^{-}][\mathrm{Br}^{-}]} = \text{constant}, K.$$

The establishment of an equilibrium in solution was one of the basic assumptions in the Ostwald theory of photographic development, but the existence of an equilibrium value at the end of development would be expected with any other mechanism. The concentration of the solution at the start of development would also be significant, regardless of the mechanism proposed. The Ostwald theory of development, however, assumes a rapid enough exchange between a silver bromide grain and the solution during development for the procedure to be governed by the concentration of the silver in solution, whereas in most of the other mechanisms the changes inside the grain are considered significant for the rate of development. This kinetic aspect is treated in the preceding chapter. It does not affect the thermodynamic considerations discussed in these paragraphs. In the experiments mentioned, the equilibrium values were determined by varying the concentrations of only Fe^{--} and Fe^{-}. The same applies to the values for K (685, 674, and 653), which were obtained at a dilution of 100 cc. by another interesting method.

The photographic plates carrying developed images are placed in a solution of ferri-oxalate and potassium bromide, and the silver bromide formed is determined. Thus, if the original density is D_0 and the final density is D, if m and n are the factors for converting densities into concentrations of ferrous and ferric ions and bromide. respectively, and A is the plate area,

$$\frac{m \text{ or } n(D_0 - D)A}{100}$$

is the change in concentration. Calling this c or c',

$$\frac{\text{Fe}^{--} + c}{(\text{Fe}^{-} - c)(\text{Br}^{-} - c')} = K.$$

This method gives only an upper limit to the equilibrium constant; near the equilibrium point the reaction proceeds very slowly, and atmospheric oxidation, though reduced as far as possible, introduces large errors.

The bromide concentration in these experiments at a dilution of 100 cc. was again constant and identical with that recorded in Table XV.* However, a variation in the concentration of the bromide from $N/10$ to $N/50$ again gave (with the balancing method) K values of 686, 670, and 682.

Other ferrous salt-containing developers with organic acids are made with the lactate, salicylate, citrate, tartrate, and formate. They are less effective, however, than the oxalate developer, particularly the last three mentioned. These developers are used in slightly acid solutions, the amount of acid having no effect on the rate of reaction unless it is very high.[10] Ferrous succinate is recommended for use in slightly ammoniacal solution. Some developers of this type described by Carey Lea [11] are on the alkaline side. As a developer containing a cuprous salt with an organic acid, the ammoniacal cuprous oxalate [6] might be mentioned.

The stability of complexes formed by the ferric-ion with citric acid, $Fe_2(C_6H_5O_7)_3^{---}$, malonic acid, $Fe(C_3H_2O_4)_3^{---}$, and oxalic acid, $Fe(C_2O_4)_3^{---}$, has been confirmed by means of potentiometric titrations.[12] The same investigation proved that the tendency of the ferrous ion to form complexes with these acids is comparatively negligible.

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* In Table 4, "Investigations on the Theory of the Photographic Process," Sheppard and Mees, the decimal point in one of the vertical columns is misplaced; according to the values given there, K would be 71 instead of 710. Since the ratio of Fe^{--} : Fe^{-} is stated to be 36, the error must be in the bromide, the concentration of which should be 0.00101, not 0.0101.

INORGANIC NON-METAL-CONTAINING DEVELOPING AGENTS

Sodium hydrosulfite, $Na_2S_2O_4$, was first mentioned as a developing agent by Eder[13] and repeatedly investigated later.[14] The solutions are very unstable. They absorb atmospheric oxygen rapidly in a reaction which seems to be catalyzed by silver particles, and, in the absence of air, the developer deteriorates by the reaction

$$3\,Na_2S_2O_4 \rightarrow 2\,Na_2S_2O_3\ \text{(thiosulfate)} + Na_2S_2O_6\ \text{(dithionate)}.$$

Moreover, the developer made up with an equal weight of sulfite and the usual bromide content fogs chloride and bromide emulsions considerably; *i.e.*, it does not discriminate sufficiently between exposed and unexposed grains, and the fog increases with the acidity of the solutions. The developer is, however, according to Lüppo-Cramer,[15] suited for the processing of iodide emulsions. It is, therefore, an interesting example of an inorganic developer which is too active for the usual emulsions but suitable for one which is more difficult to develop. The situation is, on another level, similar to that in which the ordinary developers fog emulsions prepared with an excess of silver ion or fog gelatin-free silver bromide layers, while weaker developers produce images in these layers.[16]

The disadvantages of sodium hydrosulfite are not overcome by using the mixture of formaldehyde sodium sulfoxylate (Rongalite C) and sodium bisulfite, which forms sulfoxylate and hydrosulfite:[17]

$$NaHSO_2CH_2O + NaHSO_3 \rightarrow NaHSO_3CH_2O + NaHSO_2,$$
$$NaHSO_2 + NaHSO_3 \rightarrow Na_2S_2O_4 + H_2O.$$

Unlike Rongalite C alone, which does not act as a developer, these solutions develop; but their behavior is the same as that of solutions of sodium hydrosulfite itself.

A solution of sodium hydrosulfite and sodium bisulfite with a high content of potassium bromide, which is readily prepared from the mixture of these salts and is stable in the dry state, is described by Seyewetz[18] as a good desensitizing developer for several negative emulsions. White and Weber[19] mention a developer containing 20 grams of sodium hydrosulfite, 30 grams of sodium bisulfite, and 7 grams of potassium bromide per liter as an energetic inorganic solution which develops little fog unless development is prolonged, and Brooks and Blair[20] describe a hydrosulfite developer which is activated by cysteine.

Sodium sulfite itself in carbonate alkaline solution, according to Schaum and Braun,[21] is a developer. Its action is so slow, however, that it cannot play a role in the usual sulfite-containing developers. The observation that the developing agent under an atmosphere of hydrogen is of still lower activity than in the presence of air may indicate that the action of sulfite as a developer is connected with its autoxidation as a coupled reaction. According to Beukers,[22] sulfite in the presence of 0.01 N potassium bromide at 25° C. does not reduce silver bromide.

Hydrogen peroxide, $HO—OH$, hydroxylamine, $H_2N—OH$, and hydrazine, $H_2N—NH_2$, are particularly interesting non-metal-containing inorganic developers, because they can be considered the direct combinations of the "effective groups" of the most important organic developers.[23] Hydrogen peroxide acts as a developer in rather strongly alkaline solution and produces an image in about five to ten minutes.[24] Without alkali it does not develop.

Hydroxylamine was first described as a developing agent by Egli and Spiller[25] and further investigated by Sheppard and Mees,[26] Nichols,[27] and James.[28] It is a weak developer in alkaline solution, forming bubbles in the emulsion, obviously of nitrogen and nitrous oxide.

Hydrazine was shown by Andresen[23] to be a weak developer in strongly alkaline solution. It also forms bubbles of nitrogen in the emulsion.

ORGANIC DEVELOPING AGENTS WITHOUT METALS

The first group of organic non-metal-containing developing agents to be discussed are the homologues of the inorganic substances mentioned above, in which one or more hydrogen atoms are replaced by organic radicals (see (A) below). Such derivatives of hydrazine, $H_2N—NH_2$, are, for instance, phenylhydrazine, -NH—NH$_2$, and hydrazobenzene,

-NH—NH- ;

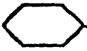
of hydroxylamine, H$_2$NOH, phenylhydroxylamine,

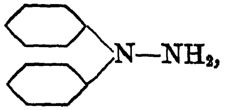
-NHOH.

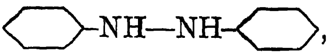
These developing agents contain the undivided radicals of the inorganic developers as characteristic groups to which they owe their reducing properties. No developing agent of outstanding importance has been found among these compounds. The practically important developing agents may formally be considered as derived from hydrogen peroxide, hydrazine, and hydroxylamine by inserting an organic divalent radical between the two hydroxyl or the two amino groups, or between the hydroxyl and the amino group, respectively (see (B) below). They are not homologues of their inorganic prototypes, since they contain the radicals of the inorganic developers not as such, but "split" into the amino and hydroxyl groups. The inserted organic divalent radical, however, as is shown later (p. 359), must fulfill certain conditions for the resulting compounds to develop the latent image; and these conditions are such as to establish a closer than formal resemblance to the inorganic prototypes.[29] Among the compounds (see (B) below), some organic developing agents of different types are discussed, which, though unimportant in practical use, are interesting theoretically.

(A) No data indicate that organic peroxides have developing properties under conditions where hydrolysis with formation of hydrogen peroxide is excluded.

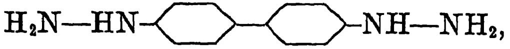
A. and L. Lumière and Seyewetz[30] tested phenylhydroxylamine, -NHOH, soon after its discovery and found the aqueous solution to be a developer. This solution is alkaline because of the properties of phenylhydroxylamine itself and, at variance with the isomeric *p*-aminophenol, no addition of alkali is necessary or even desirable, since it promotes fog. However, the addition of 1 to 4 per cent of sulfite improves the power of the developer, obviously by increasing the pH; and the formation of fog can be hindered by the addition of bromide. *o*- and *p*-tolylhydroxylamines and *o*- and *p*-xylohydroxylamines [31] show similar properties. The aliphatic hydroxylamines,* dimethyl-, diethyl-, and di-β-hydroxyethyl-hydroxylamine with the formulas R_2NOH ($R = —CH_3, —C_2H_5, —CH_2—CH_2—OH$), act as weak developers in 0.5 per cent solutions which contain 4 per cent sulfite and 0.5 per cent sodium hydroxide. The particular use of phenylhydroxylamine oxalate as a developer and in developers became the subject of patents in 1921, 1924, and 1928.[32]

In 1885, Jacobsen [33] disclosed as developing agents phenylhydrazine, -$NH—NH_2$, various hydrazines of benzene homologues, α- and β-naphthylhydrazine and, later on,[34] aliphatic hydrazines and carboxylic acids of aromatic hydrazines. Votoček [35] added to this list diphenylhydrazine,

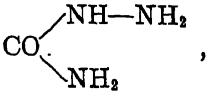


hydrazobenzene, 

, dihydrazinodiphenyl,

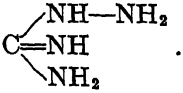


, aminourea,



$$CO\begin{matrix}NH—NH_2\\NH_2\end{matrix},$$

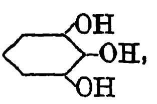
and aminoguanidine,



$$C\begin{matrix}NH—NH_2\\=NH\\NH_2\end{matrix}.$$

(B) The substances to be discussed next are those which may be considered derivatives of "split" hydrogen peroxide, hydroxylamine, or hydrazine. Among these are all the important organic developing agents.

Pyrogallol,



was the first compound belonging to this group which was found to have developing properties. Archer[36] used it in 1850 and

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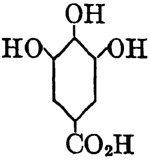
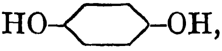
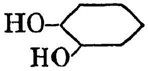
* P. W. Vittum, private communication.

Regnault and Liebig[37] in 1851 to develop wet collodion plates in an acid solution; and when gelatin dry plates were introduced, its alkaline solution was found to be a useful developer for silver bromide emulsions. Gallic acid,

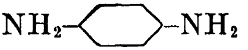
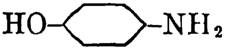


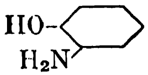
on the other hand, which had been introduced into photography in 1840,[38] does not develop gelatin dry plates. Under extreme conditions (2 per cent developing agent, 2 per cent sulfite, 1 per cent sodium hydroxide, 5 minutes at 43° C.), it can be made to develop gelatino-silver chloride paper.*

Hydroquinone, , was described as a developing agent in 1880 by Abney;[39] catechol,

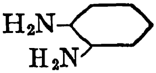


,

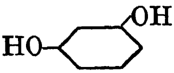
by Eder and Toth in 1880.[40] Andresen discovered that *p*-phenylenediamine,  (1888),[41] *p*-aminophenol,  (1891),[42] *o*-aminophenol,



(1891), and *o*-phenylenediamine,



(1891),[42] are developing agents. On the other hand, resorcinol,



(Eder and Toth, 1880), *m*-aminophenol, and *m*-phenylenediamine (Andresen, 1891) do not develop the latent image. The test to which the materials were subjected is illustrated by the following quotation:

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* P. W. Vittum, private communication.

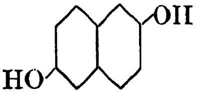
> "A silver bromide plate which had been given the right exposure under a contrasty negative, after three minutes did not show any trace of an image with a solution of resorcinol (1 : 50) to which had been added 4 mol sodium hydroxide."

The properties of these developing agents vary considerably with the conditions of the solution. Hydroquinone, for instance, is not a useful developer for silver bromide in acid solution, and in alkaline media the rate of development increases greatly with the pH. The dependence of developing properties on the pH is different with *p*-aminophenol and with *p*-phenylenediamine, which, in turn, differ from each other. Amidol, on the other hand, develops even when acid and other substances which have been described as lacking in developing properties under normal conditions acquire them in very strongly alkaline solutions.

Attempts to establish the relationship between chemical constitution and developing properties of organic compounds were made simultaneously by A. and L. Lumière[43] and by Andresen[23,42,44] in 1891. The results of these papers may be combined as follows:

1. Compounds of the aromatic series which develop the latent image contain at least two hydroxyl, or two amino, or one hydroxyl and one amino group.
2. In benzene derivatives, these groups must be in the *o*- or *p*- positions to each other. The corresponding *m*- compounds are not developing agents.
3. Substitution of hydrogen atoms in the amino groups by alkyl groups does not injure the developing property, while it is destroyed by the same substitution in the hydroxyl groups.
4. Substitution of hydrogen atoms in the ring by further hydroxyl or amino groups, alkyl groups, or halogen atoms, does not interfere with the developing properties of the compounds.
5. For polynuclear aromatic compounds, the same rules apply; *i.e.*, the additional nucleus acts as an alkyl substituent. However, in some cases the characteristic groups may be distributed between the nuclei; for instance, 2,6- and 1,5-dihydroxynaph-

thalene,



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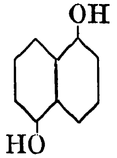


,

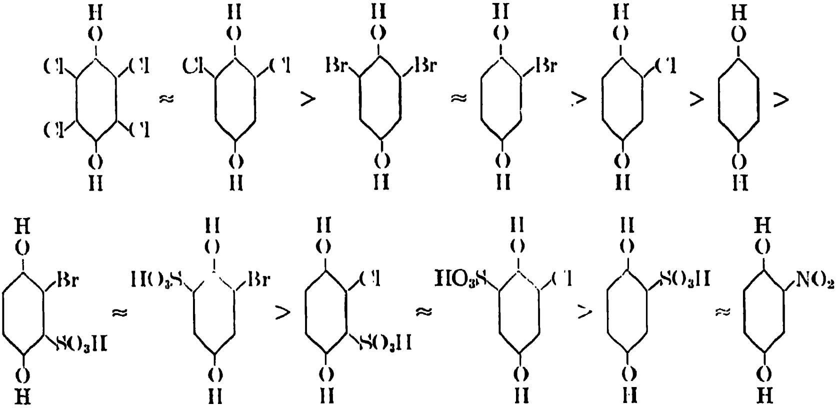
are developers.

These rules are illustrated and amplified by the following:

The effect of various substituents in the hydroquinone nucleus is shown by Table XVI, which has been compiled from an article by A. and L. Lumière and Seyewetz[45] wherein these authors summarize their work on the subject:

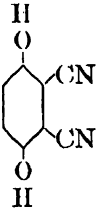
TABLE XVI

Relative Developing "Power"



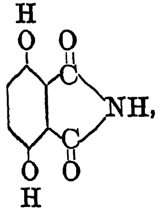
(≈ = almost equal.)

The authors state, furthermore, that toluhydroquinone is more powerful than hydroquinone and that dinitrohydroquinone is not a developing agent. According to Pavolini,[46] dicyanohydroquinone,

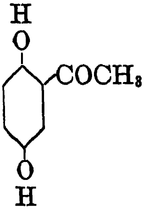
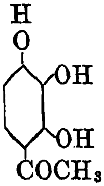
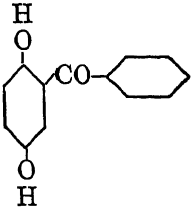


,

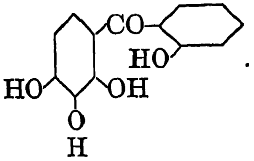
and dihydroxyphthalimide,



do not develop the latent image. In another paper, A. and L. Lumière and Seyewetz[47] deal with ketones like

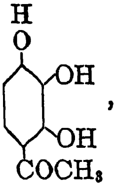




and

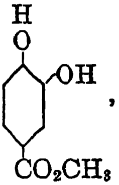


Substitution of the keto group in the nucleus of a developing agent does not appreciably change the power of the developer if the keto group has an aliphatic radical or an aromatic radical which is not substituted by hydroxyl. Hydroxyl in the second nucleus, without regard to its position, is said to destroy the developing action.

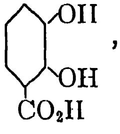
Gallacetophenone,



behaves in a manner similar to methyl or ethyl gallate. These gallic acid esters and the acid amide, gallamide,[48] are developing agents similar to pyrogallol, whereas the acid itself develops only under extreme conditions (p. 341). Catechol, protocatechuic ester,

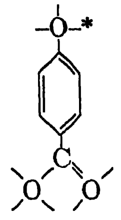


protocatechuic amide,[48] and protocatechuic aldehyde [49] are developing agents of normal strength; and the acid is reported not to be a developing agent. The difference between the esters and the acids, according to Homolka,[50] is not explained by the acid function as such, since the influence of the sulfonic acid group on the developing action is much smaller than that of the carboxylic acid group. The effect of the latter might be understood if it masked a hydroxyl group in the para position. Homolka justly rejects the possibility that the carboxylic acid group forms an ester with the hydroxyl group in the para position because this is unlikely to exist in alkaline solution and is impossible for steric reasons. However, according to Armstrong, James, and Weissberger,[51] the divalent ions of *p*-hydroxyphenyl carboxylic acids can be formulated with the benzenoid constitution I and with the quinonoid constitution Ia (p. 346). Both forms, according to the theory of resonance, contribute to the structure of the divalent ion and thus stabilize this ion and mask the hydroxyl group in para position to the carboxylic group. With the divalent ions of the analogous sulfonic acids, no resonance of a similar degree exists. A double bond between the sulfur atom and the carbon atom to which it is attached is very improbable, because it would increase the number of covalent bonds of the sulfur beyond four. On the other hand, catechol *o*-carboxylic acid,

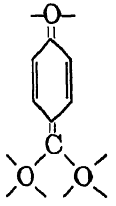


which has no carboxylic group in para position to the hydroxyl group, also is a weak developing agent and thus exhibits the masking effect of the carboxylic acid group on a hydroxyl group; hydroquinone monocarboxylic acid (gentisic acid) shows the same behavior. Here, obviously, an ortho-quinonoid structure, II (p. 346), stabilizes the ion and masks the hydroxyl group in ortho position. In this connection, it may be mentioned further that the strong depression of the developing activity of hydroquinone by the introduction of a nitro group is also accounted for by the possibility of resonance, namely, between the forms

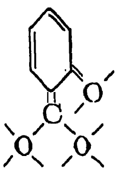
III and IIIa of the doubly charged ion.



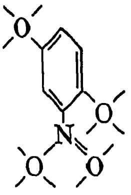
I



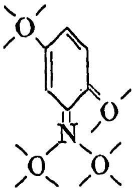
Ia



II



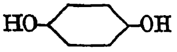
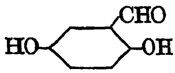
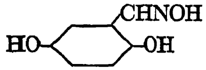
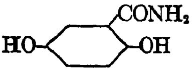
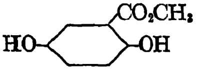
III



IIIa

Some comparative data on gentisic acid and its derivatives, which exhibit behavior similar to that of the protocatechuic and gallic acids and their derivatives, are given in Table XVII.[51]

TABLE XVII

Developing Agent		*Developing Rates* × 10^2
Hydroquinone		10.5
Gentisic aldehyde		3.75
Gentisic aldoxime		6.0
Gentisic acid amide		9.4
Gentisic acid methyl ester		4.45

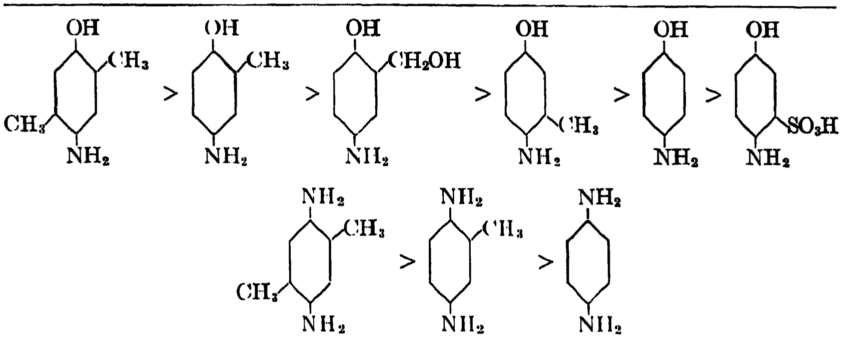
The developing rates were determined with a normal motion-picture positive emulsion as the slope of the γ, t curves at $\gamma = 1.5$, the developing agent (0.01 mol) being used in a solution containing sodium sulfite, 16.0 grams; sodium carbonate, 16.0 grams; and potassium bromide, 0.4 gram per liter (pH 10.6). Gentisic acid is too inactive a developer for a good test to be obtained in the preceding formula. A rough test, employing a caustic formula and silver chloride developing-out paper as the photographic material, indicated that the development rate with this agent is only about one-tenth that of hydroquinone monosulfonic acid under the same conditions.

* – indicates two electrons.

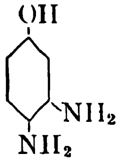
Results similar to those registered in Table XVI were obtained when the influence of substituents was studied in *p*-aminophenol and in *p*-phenylenediamine.[52,53,54,55] *p*-Aminoxylenol reduces not only the exposed grains, but rather strongly also the unexposed ones.

TABLE XVIII

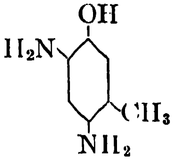
Relative Developing "Power"



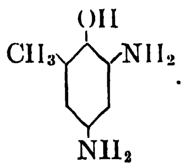
Of the compounds which combine more than two OH and NH_2 groups,



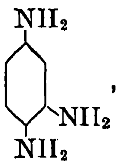
and



are of about equal developing power but are surpassed by

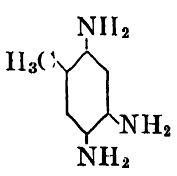


· 1,2,5-Triaminobenzene,



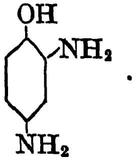
,

is a strong developer if the hydrochloride is added to sodium sulfite solution, and still stronger is

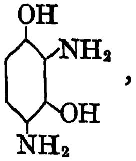


,

which is about equal to amidol,

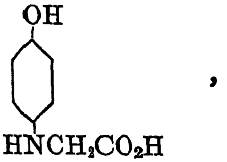


The latter produces an energetic developer even without alkali, and 2,4-diaminoresorcinol,

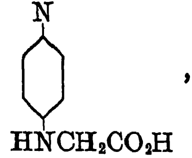


has the same property.[55] 2,4,6-Triaminophenol and 2,4,5-triamino-3-hydroxyphenol are said to develop only weak images. The explanation that development is stopped by the oxidation products is not very plausible, and a reinvestigation of the compounds used might be warranted.

With *p*-aminophenol and *p*-phenylenediamine, besides substitution in the nucleus, replacement of hydrogen atoms in the amino groups offers possibilities for variation. *p*-Hydroxyphenylaminoacetic acid, photographic "glycin,"

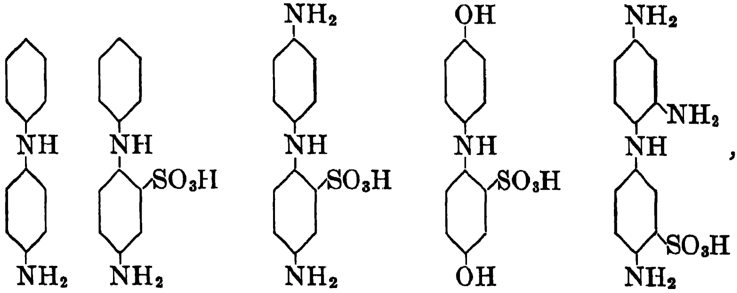


is weaker as a developer than *p*-aminophenol. The acid amide of this compound is described as an energetic developing agent.[56] *p*-Methylaminophenol is a stronger developing agent than *p*-aminophenol, and the alkyl *p*-phenylenediamines[57] and their glycine derivatives,[58] *e.g.*,



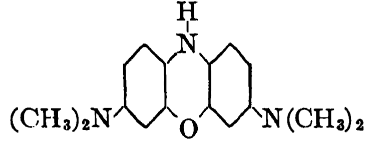
are claimed to be stronger than the parent substance.

Desalme[59] and A. and L. Lumière and Seyewetz[60] investigated numerous derivatives of *p*-phenylenediamine and *p*-aminophenol in which a hydrogen of the amino group was replaced by an aromatic system. Sulfonation was used to counteract the loss in solubility with the increasing size of the molecules.



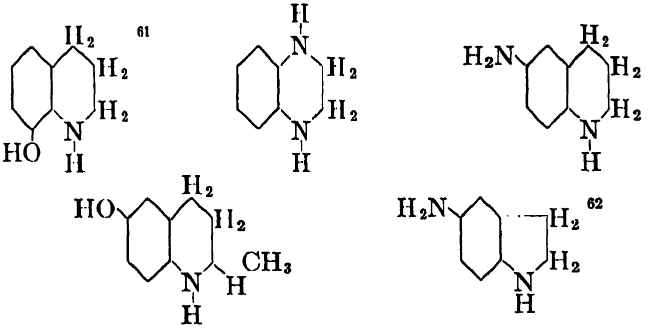
, etc.

(Pyramidol)



Phenyl substitution of the amino group markedly diminished the energy of the developer but did not destroy it. The introduction of amino and hydroxyl groups into the benzene nuclei augmented the developing energy. A further linkage between the nuclei by oxygen (or sulfur or the imino group), as in the last example, destroyed the developing property, in spite of the fact that compounds with the formulas so obtained form quinonoid products when oxidized (p. 355).

An interesting class of developing agents in which one of the characteristic groups is part of a heterocyclic nucleus is illustrated by the following examples:



The 1,2-, 2,1-, and 1,4-aminonaphthols, and 1,2- and 1,4-diaminonaphthalenes are developing agents. 1,5-Diaminonaphthalene is not a developing agent.[63] An investigation of the dihydroxynaphthalenes is described on p. 356.

The following rules which regulate the *power* of developing agents were summarized by Nietz[64] from the papers by A. and L. Lumière and Seyewetz and Andresen:

1. Developers having the two groups (OH, OH; NH_2, NH_2; OH, NH_2) in the para position are more powerful than those in which the groups are in the ortho position.
2. The dihydroxybenzenes are more powerful than the aminophenols, which, in turn, are more powerful than the diaminobenzenes.
3. Substitution of acid groups (COOH, SO_3H, etc.) for hydrogen in the benzene nucleus lowers the energy of the developer.
4. Substitution of chlorine or bromine for hydrogen in the benzene nucleus increases the developing energy.
5. With two hydroxyl groups only, alkali is needed.
6. With two amino groups only or with one $-OH$ and one $-NH_2$ group, the developer functions without alkali.
7. If the reducing agent contains a mixture of three or more $-OH$ and $-NH_2$ groups, the developing energy is greater without alkali than it is with alkali when the developing function exists singly.
8. Substitution of an alkyl group in the $-NH_2$ group of an aminophenol raises the (photographic) reduction potential.
9. If the $-NH_2$ group of an aminophenol or diamine is substituted to give a glycine, the (photographic) reduction potential is lowered.

Terms like "activity," "power," and "strength" are equivocal if used to characterize chemical substances, even if they are applied to a definite reaction. They may refer to the rate at which the reaction proceeds or to the degree of completion which a reaction, particularly a reversible reaction, reaches. The *rate* of development is discussed in Chapter XI, and the *electrochemical reduction potentials* of developing agents, in Chapter XII. Great difficulties arise in the measurement and in the interpretation of these potentials because of the instability of the oxidation products and the ensuing irreversibility of the systems. Furthermore, the significance of these potentials is limited because they are only one of the various factors which are important in development.

Methods of obtaining *quantitative* data on developing agents under more "natural" conditions were therefore used by Sheppard[65] and by Nietz. These methods are discussed in detail in Chapter XI, since they involve the kinetics of development, but it is convenient to mention them briefly here so that the results may be applied to the developing agents discussed in this chapter.

Abegg[66] proposed that the reducing energy of a developer should be characterized by the concentration of bromide it could just overcome. According to Sheppard, however, this method cannot be used for organic reducers. Sheppard, therefore, determined the depression of density produced at a given degree of development for a given concentration of bromide and compared it with the depression produced by bromide in ferrous oxalate developer:

> "For this, the numerical relations were known. ΔD, the constant depression, is proportional to the concentration of bromide ion and inversely proportional to the time of development. Hence, if the depression with the other (organic) developer be measured, then the concentration of bromide necessary to produce with ferrous oxalate the same depression at the same degree of development γ can be calculated, and this affords a numerical comparison of the developing energy compared with ferrous oxalate."

Sheppard's results for the concentration of bromide producing the same retardation as N/100 bromide with ferrous oxalate are given in the following table:

TABLE XIX

Developing Agent	*Bromide Concentration*
Ferrous oxalate, $Fe(C_2O_4)_2$	0.01 N
Hydroxylamine, NH_2OH	0.0113 N
Hydroquinone, $C_6H_4(OH)_2$	0.0052 N, 0.0073 N
p-Aminophenol, $C_6H_4(OH)NH_2$	0.034 N

Nietz used a more elaborate procedure to determine *relative reduction potentials*, which, in distinction to the electrochemical reduction potentials, are designated as *bromide potentials*. The power of a developer is measured by the concentration of bromide required to produce a given change. The mechanism of the bromide action is connected by Sheppard and Nietz, on the basis of Abegg's theory of photographic development, with the decrease of silver ions in solution caused by the bromide ions. The assumption that the bromide acts by its adsorption to the grains and that the developer has to work against this hindrance is more in agreement with recent evidence. However, Nietz himself states that

> "taking all the evidence into account, it is not justifiable to assume that it (the decrease in the concentration of silver ion) is ever the only effect or always the chief one."

Tables XX and XXI give the bromide potentials (π_{Br}) determined by Nietz and show the compounds arranged according

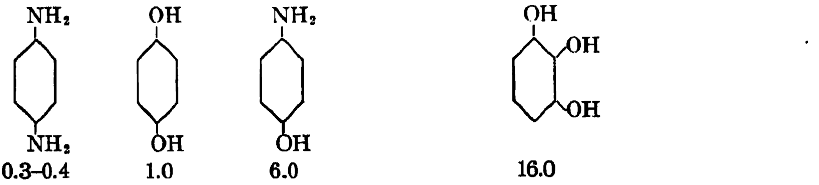
TABLE XX

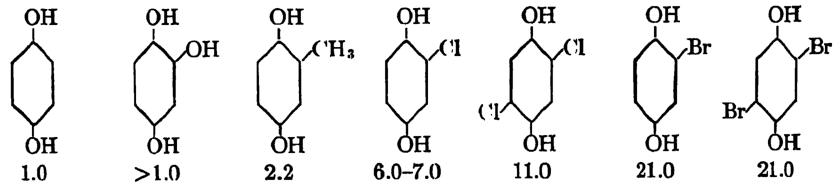
Relative Reduction Potentials (Bromide Potentials)

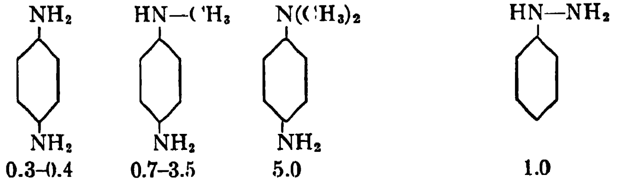
	π_{Br}
Ferrous oxalate	0.3
p-Phenylenediamine hydrochloride, no alkali	0.3
p-Phenylenediamine hydrochloride, plus alkali	0.4
N-Methyl-*p*-phenylenediamine hydrochloride, no alkali	0.7
Phenylhydrazine	<1.0
Hydroquinone	1.0
2-Hydroxyhydroquinone	>1.0
p-Hydroxyphenylglycine (glycin)	1.6
Hydroxylamine	2.0
Toluhydroquinone	2.2
N-Methyl-*p*-phenylenediamine hydrochloride, plus alkali	3.5
N-Dimethyl-*p*-phenylenediamine hydrochloride	5.0
p-Hydroxydiphenylamine	<6.0
o-Hydroxymethyl-*p*-aminophenol	<6.0
o-Methyl-*m*-isopropyl-*p*-aminophenol	<6.0
p-Aminophenol	6.0
Chlorohydroquinone (Adurol-Hauff)	6.0–7.0
Pyrocatechol	7.0
p-Amino-*o*-cresol	7.0
p-Amino-*m*-cresol	9.0
Dimethyl-*p*-aminophenol sulfate	10.0
Dichlorohydroquinone	11.0
Pyrogallol	16.0
Methyl-*p*-aminophenol sulfate (metol)	20.0
Bromohydroquinone (Adurol-Schering)	21.0
Dibromohydroquinone	21.0
p-Methylamino-*o*-cresol	23.0
2,4-Diaminophenol (Amidol), plus alkali	30–40
Thiocarbamide (Thiourea)	50

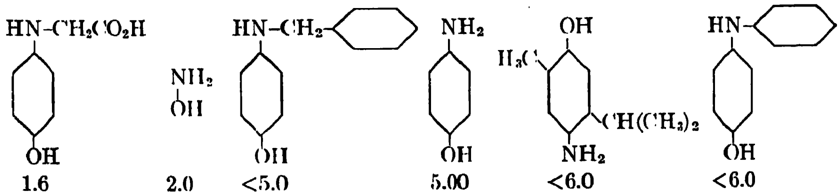
TABLE XXI

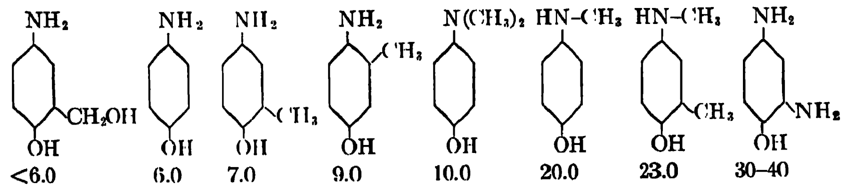
RELATIVE REDUCTION POTENTIALS (BROMIDE POTENTIALS)







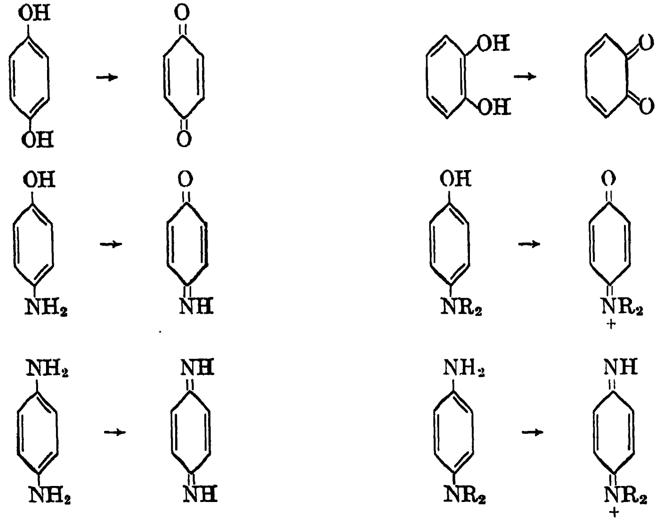




to their structures. These figures have often been quoted by writers on the subject, and probably more reliance has been placed on their quantitative significance than is justified by the facts or, indeed, by Nietz' repeated warnings. Undoubtedly, an extended study of the depression of density for different developing agents by the addition of bromide is much to be desired. On the whole, the data of Nietz' tables confirm the results of the earlier workers. They disagree, however, with the statement that the dihydroxybenzenes are more powerful than the aminophenols. The bromide potential is, in agreement with (p. 350, 4), raised by substitution of halogen for hydrogen in the benzene nucleus; and it is also raised by the introduction of alkyl groups. The position of the substituents has an influence, as shown by the two aminocresols. Introduction of alkyl groups into the amino groups of *p*-phenylenediamine and *p*-aminophenol raises the bromide potential in agreement with (8), and a differentiation according to the size or nature of the groups appears to be possible. The acidic $-CH_2CO_2H$ group, however, lowers the potential in accordance with (9).

TABLE XXII

REDUCED AND OXIDIZED STATES (SIMPLIFIED) OF SOME DEVELOPING AGENTS

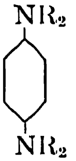


Properties of chemical compounds may be exhibited by the compounds as such; *e.g.*, color, crystal form, vapor pressure, melting point, or they may become evident only while the compound changes its chemical individuality. The property of being a developing agent belongs to the latter class. The significance for that property of the chemical changes which a compound can undergo has been discussed by several authors. It is considered in the following paragraphs, together with those compounds which, by the rules given on page 350, would not be expected to be developing agents, though a more fundamental discussion would explain their developing property.

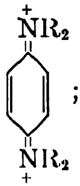
Andresen[42] points out that aromatic para-dihydroxy, -diamino or -hydroxyamino compounds, which are developing agents, form quinone or quinonoid substances when oxidized and that the ability of the ortho derivatives to develop the latent photographic image is connected with the fact that they, too, form quinonoid oxidation products.

The simple benzenoid developing agents with their quinonoid oxidation products are listed in the following table to illustrate the fundamental possibilities. The actual fate of the developing agents in a developer, which is usually much more complex, is discussed in Chapter X, as far as it has been investigated.

With tetra-alkylamines,

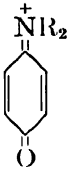


might form



;

it is probable that the loss of one or both of the amino groups occurs, and



and quinone result.

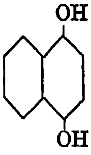
The tendency of oxygen to form oxonium-ion is so much weaker than that of nitrogen to form ammonium-ion that O-alkyl substituted hydroxy compounds do not develop, while the tertiary N-dialkylated amines are powerful developing agents.

According to Desalme,[67] developing agents are capable of quinone formation and of condensation with their quinonoid oxidation products, and Abribat[68] suggests that substances act as developers if they are capable of forming quinonoid compounds on oxidation, even if they do not follow Lumière's and Andresen's rules. However, the experiments of Abribat[68] and Langer,[69] showing that leuco bases of triphenylmethane dyes, *e.g.*, of malachite green and fuchsin, are developing agents, could not be repeated by other authors.[70]

These statements concerning the connection between the faculties of developing and forming quinones bring to mind the work of Luther, Leubner,[71] and Staude[72] (p. 318). These authors investigated the influence of the oxidation products of the developing agents on the initiation of development, and Staude suggested that developers are substances capable of forming addition compounds with their oxidation products. The latter property is common to many compounds which are oxidized to quinonoid products, with which the unoxidized benzenoid substances form quinhydrones or semiquinones. James and Weissberger[73] show that these semiquinones are highly reactive and that the catalytic action of the quinones in the autoxidation of hydroquinones, and possibly also in development, is due to the formation of these highly reactive semiquinones.

Andresen and Leupold[74] investigated eight of the ten possible dihydroxynaphthalenes:

1



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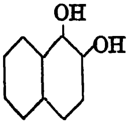

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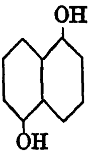
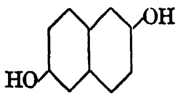
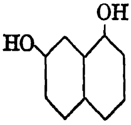


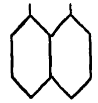
4



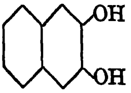
5



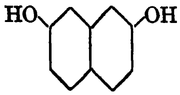
6



7



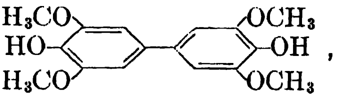
8



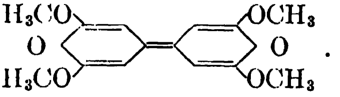
> "1 and 2 are extraordinarily energetic; 3 and 4 are of medium power; 5, 6 and 7 work slowly; 8 does not exhibit a reducing power for the latent image even on prolonged treatment."

Of these compounds, 1 to 5, and 7 can form quinones, but no 1,8- (Compound 6) or 2,7- (Compound 8) naphthoquinone can be formulated according to Kekule's theory. As expected, 8 does not act as a developer; however, 6 constitutes an exception to the quinone rule.

Analogous to the dihydroxynaphthalenes, in which the hydroxyl groups are not attached to the same nucleus, is the case of hydrocoerulignon,

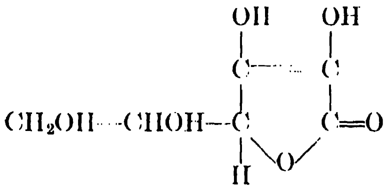


which is obviously a developer[75] owing to the ease with which it is oxidized to coerulignon,

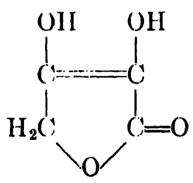


p-Diphenol, on the other hand, does not develop under the same conditions. The methoxy groups strongly enhance the developing properties of the compound. The example of hydrocoerulignon fits the quinone rule perfectly. On the other hand, it is not in agreement with the suggestion[23] that in a polyunuclear developing agent at least two hydroxyl groups must be attached to the same nucleus, just as various dihydroxynaphthalenes do not obey this rule.

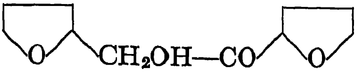
To the developing agents with pairs of hydroxyl or amino groups, or a hydroxyl and an amino group, attached to aromatic systems, there have been added in recent years a number of aliphatic compounds. A solution of ascorbic acid



develops slowly in the absence of alkali; in the presence of sulfite and carbonate, it is a useful developer.[76] Oxytetronic acid[76]

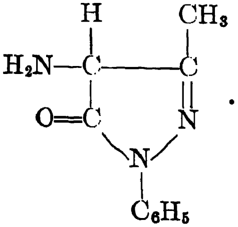


and furoin[73a]

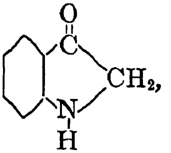


have developing properties with some silver chloride emulsions, and dihydroxyacetone $CH_2OH—CO—CH_2OH$[51] develops in caustic alkaline solution. The latter two substances act as reducers in their ionized enolized form,[77] containing the group —COH═COH—. Hence, it is evident that all the substances just mentioned are aliphatic analogues of the aromatic *o*-dihydroxy compounds.

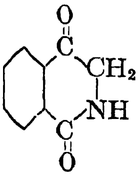
The aliphatic analogues of the *o*-aminophenols and the aromatic *o*-hydroxyamines in general are the α-aminoketones. These compounds contain the group $—CO—CHNH_2—$, which is in tautomeric equilibrium[78] with $—COH═CNH_2—$, and were disclosed as developers by Eggert and Wendt.[79] As examples, among others, are mentioned diethylaminoacetone, $(C_2H_5)_2N—CH_2—CO—CH_3$; aminoacetic acid ethyl ester, $H_2N—CH_2—CO_2—C_2H_5$, and 1-phenyl-3-methyl-4-amino-5-pyrazolone,



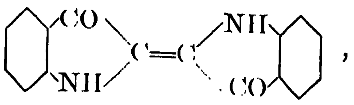
Indoxyl,



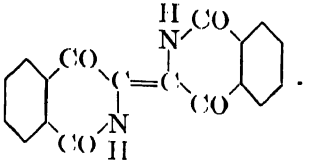
and 4-hydroxyisocarbostyril,



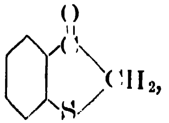
which Homolka[80] describes as developers, are substituted α-amino ketones and therefore are mentioned here. In development, they form indigo,



and carbindigo,



However, according to the same author, thioindoxyl,



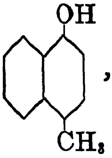
is also a developer, and this suggests the possibility that indoxyl and hydroxycarbostyril owe their properties as developing agents to other factors than their being α-amino ketones (p. 361).

Kendall[81] extends the analogy between the aromatic and the aliphatic developing agents with pairs of $-OH$ and $-NH_2$ groups or an $-NH_2$ and $-OH$ group, and formulates a rule which covers both types: Substances can be developers if they have the formula $\alpha\text{-}(C{=}C)^n\text{-}\alpha'$, where α and α′ are $-O-$ and $-N<$, and $n = 0$ or a whole number. The case $n = 0$ embraces hydrogen peroxide, hydroxylamine, and hydrazine; the case $n = 1$, pyrocatechol, *o*-aminophenol, *o*-phenylenediamine, ascorbic acid, hydroxytetronic acid, the α-ketols, the α-amino ketones, and others; and the case $n = 2$, hydroquinone, *p*-aminophenol, and *p*-phenylenediamine, whereas hydrocoerulignon is a representative of the case $n = 3$. Kendall's rule can be expressed by the statement that hydrogen peroxide, hydroxylamine, hydrazine, and their vinylologues can be developers. When oxidized, the α-hydroxy ketones and the α-amino ketones form α-diketones,

$$R-COH{=}COH-R \rightarrow R-CO-CO-R$$
$$R-COH{=}CNH_2-R \rightarrow R-CO-CO-R;$$

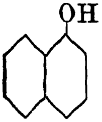
and Ostromislenski[82] drew attention to the analogy between the α- and γ-diketones and the o- and p-quinones and extended the quinone rule [42,67,68] to include the aliphatic substances. The existence of compounds of an oxidation state between α-hydroxyketones and α-diketones which are analogous to the quinhydrones or semiquinones[83] further justifies the extension of the quinone rule to the aliphatic series.

However, there are developing agents which do not adhere to Kendall's rule or, at first sight, to the quinone rule: Naphthohydroquinone monomethyl ether is a usable developing agent[84] and, under rather extreme conditions (2 per cent developing agent, 2 per cent sulfite, 1 per cent sodium hydroxide, 5 minutes at 43° C.), 4-methyl-1-naphthol,



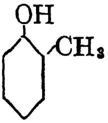
,

and α-naphthol itself,



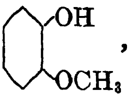
,

develop chloride paper. Under the same conditions, o-cresol,



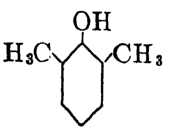
,

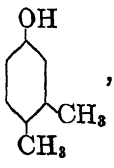
catechol monomethyl ether,



,

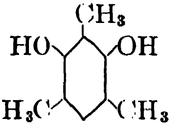
and some xylenols,



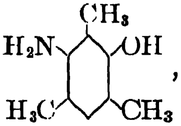


,

show traces of development; and Homolka[85] describes dihydroxymesitylene and hydroxyaminomesitylene,

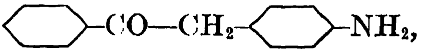


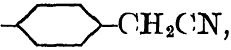
and

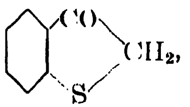


,

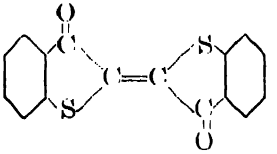
as developing agents. A. and L. Lumière and Seyewetz confirmed this result for the former compound[86] but could not repeat it with the latter. Phenyl-4-aminobenzyl ketone,



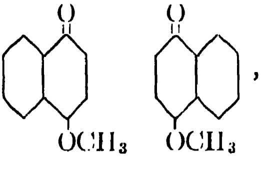
and *p*-aminophenylacetonitrile,  are reported to have weak developing properties.[51] Homolka also discovered that thioindoxyl,[80a,85]



acts as a developing agent and forms thioindigo,

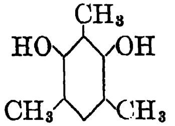


and the developing properties of indoxyl and hydroxycarbostyril, which on development form indigo and carbindigo, may here be mentioned again. It is known that naphthohydroquinone monomethyl ether when oxidized also forms a dimeric "indigoid" condensation product, the *o,o'*-binaphthoquinone derivative,[87]

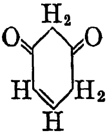


and that the other compounds, including 1,8-dihydroxynaphthalene, undergo similar condensations or are oxidized to mononuclear quinones. Their developing action may therefore be linked to this reactivity. However, further work on the mechanism of the oxidation of these unusual developing agents is required to decide whether or not their developing action follows the quinone rule.

Further investigations should also clarify why substituents such as methyl groups transform a nondeveloper, for instance, resorcinol, into a developer, dihydroxymesitylene,



Homolka offered the suggestion that resorcinol undergoes a tautomerization to the diketo form,



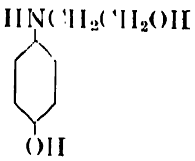
which does not develop, and that the methyl groups prevent this tautomerization. However, the activation by the methyl groups might also be caused by their electron-releasing influence. When a reducing agent is oxidized, it loses electrons, which are transferred to the reduced substance. Substituents and other changes which loosen the electrons of the reducing agent and facilitate their transfer therefore assist; substituents which restrain electrons hinder this reaction. Inasmuch as the ion of the reducing agent is the reactant proper, the effect of substituents on the dissociation constant must, furthermore, be of importance.

With respect to the influence on the electrons, it may be expected that substituents of the first order will increase the energy of the developing agents, because it is these which make electrons available and therefore direct newly introduced substituents into ortho and para positions. Substituents of the first order are alkyl groups, amino and alkylamino groups, hydroxy and alkoxy groups, and halogen. Substituents of the second order, *i.e.*, those withdrawing electrons from the remainder of the molecule, such as $-CO_2H$, $-SO_3H$, $-SO_2-$, and NO_2-, would be expected to diminish the energy of developing agents. It is obvious from the examples and rules given above that the experimental results are in fair agreement with these expectations. The specific effects of acidic and basic groups, which cause changes in the charge of the active species of the developing agent, are mentioned below. The influence of resonance between electron isomers, which stabilizes the active species of developing agents and depresses their activity, is illustrated on page 346 of this chapter. The availability of electrons is more directly measured by the redox potentials of the developing agents and developing solutions, discussed in Chapter XII.

In addition to the effects mentioned above, the substituents influence the chance which the developing agent has of coming in contact with the silver halide grains. The effect of the chemical constitution on the factors controlling this contact is discussed below. The suggestion that it depends on the formation of an addition compound between the developing agent and its oxidation products has already been mentioned.

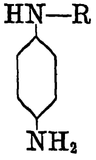
The *solubility* of the developing agents is increased by hydroxyl groups, particularly phenolic hydroxyl groups, and carboxylic or sulfonic acid groups. The acidic groups are particularly effective in alkaline solutions, where they form salts. Other solubilizing groups are of less importance. On the other hand, the solubility decreases with the growing size of the hydrocarbon residues of the molecules and, in general, with their enlargement by non-solubilizing groups.

The solubility of hydroquinone is high owing to the presence of two phenolic hydroxyl groups in the small molecule; that of aminohydroxy compounds is still sufficient in the benzene series; *e.g.*, with *p*-aminophenol. However, the suggestion has been made that groups like the hydroxyethyl radical should be introduced into the amino group,

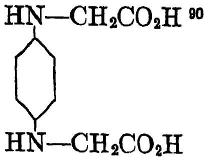


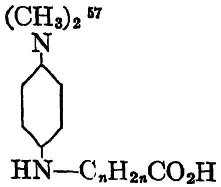
to increase the solubility, though even *p*-methylaminophenol, metol,[88] is more soluble than *p*-aminophenol itself. This effect of a simple methylation could not be predicted on the principles given above, and it illustrates the complexity of the relationship between solubility and chemical constitution. Aminophenols of the naphthalene series are too insoluble for practical use; *e.g.*, 1-amino-2-hydroxynaphthalene. However, the 6-sulfonic acid of this compound, eikonogen, and its 3,6-disulfonic acid, diogen, are developing agents of desirable qualities, owing to the solubilizing effect of the sulfonic acid group.[63]

p-Phenylenediamine and its derivatives are important as fine-grain and as color-forming developers, and various suggestions have been made for increasing their solubility; *e.g.*, by substituting solubilizing groups for hydrogen in the amino groups, as shown by the following examples:

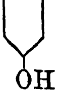


$R = —CH_2CH_2OH,\ —CH_2OCH_2OH,$[89]
$—CH_2—C_6H_4SO_3H,\ —CH_2CH_2CO_2H$





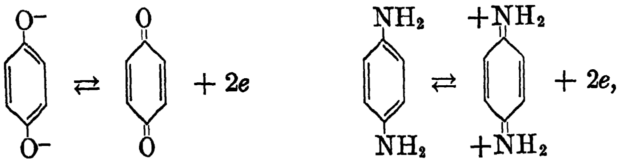
The *diffusion* of the developing agent through the gelatin layer is imperative for its reaction with the imbedded grains, and compounds like 2-lauryl hydroquinone,



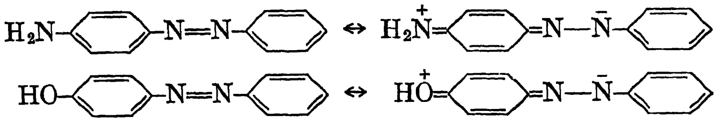
give only a trace of development at the surface of the emulsion. Low diffusibility interferes particularly with the use of a developing agent with multilayer films where a ready penetration to the lower layers is required. No special information on the problem is available from the literature. It is generally known, however, that the diffusibility decreases with increasing extension of the molecule. This extension obviously is connected with molecular weight. However, molecules of identical molecular weight may diffuse at very different rates, because a rigid molecule is more hindered by its shape than a flexible one.

The adsorption of the active species of the developing agent to the silver halide grain should be of fundamental importance (Chapter VIII, p. 316). Beyond the fact that negative charges increase the difficulty with which the anions of the developing agent penetrate the potential barrier surrounding the grains (Chapter VIII, p. 327), little is known about the influence of substituents on the adsorption of developing agents (p. 317). The decrease in developing power noted in rule 3 (p. 350) may in part be attributed to the anionic character conferred on the developing agents by the acidic groups. It should, however, not be forgotten that the acidic groups are substituents of the second order (p. 362) and that effects may occur, such as the formation of resonance hybrids (p. 346). Evans and Hanson in their papers draw attention to the fact that the hydroxyl and the amino groups, which are of signal importance for organic developing agents, are likewise characteristic of dyes as the chief auxochromic groups. They conclude that this parallelism is not a coincidence and that the reason for it is the particular faculty for adsorption which the hydroxyl and the amino groups confer on molecules. Various facts make it improbable that the essential function of hydroxyl and amino groups in dyes and developing agents is to promote their adsorption. This idea was originally suggested with respect to dyes, but it does not explain satisfactorily the function of the auxochromic groups in compounds which dye materials as different as wool and cellulose.

It is necessary to remember the existence of developing agents not having the above-mentioned groups. On the other hand, it is likely that the importance of hydroxyl and amino groups for both developing agents and dyes is not fortuitous. As shown in Chapter X, the aromatic benzenoid systems of the developing agents with hydroxyl and/or amino groups in ortho and para positions are easily oxidized, because they can be transformed into quinonoid systems,



and this property is essential for their developing action. The function of the hydroxyl or amino groups for a dye, however, may be illustrated by the examples,



which give the two resonating forms of *p*-aminoazobenzene and of *p*-hydroxyazobenzene. The behavior of these compounds as dyes is connected with their capacity for existing in two forms which are in a state of resonance. This capacity is fostered by the presence of the hydroxyl and the amino groups, because the aromatic systems substituted by them transform very easily from the benzenoid into the quinonoid state, and vice versa. Hence, it appears that developing agents and dyes have in common the property of being related to quinonoid systems. However, while the developing agents undergo a transformation into a quinonoid compound when oxidized, the dyes are in an actual state of resonance between benzenoid and quinonoid forms.

An incidental property of developing agents which has nothing to do with the developing process itself but is of great importance should be mentioned. It is the so-called toxicity of developing agents. This does not refer to the toxic effect after oral resorption of the chemicals, but to their property of sensitizing persons who handle them so that these individuals become allergic, *i.e.*, hypersensitive, to the substances, and on further contact with them develop symptoms similar to eczema. Very few cases of this type have been reported for hydroquinone; some persons are affected by *p*-aminophenol and its derivatives, for instance, methyl *p*-aminophenol. However, the most dangerous developing agents are *p*-phenylenediamine and *p*-phenylenediamine derivatives. These are also responsible for some of the cases attributed to methyl *p*-aminophenol, in which they may be present in small amounts as impurities. It is interesting to note that patents disclosing the use of solubilizing groups in developing agents claim that these groups reduce the allergenic properties of the *p*-phenylenediamine derivatives.[89]

No attempt has been made in the preceding pages to give a complete account of the compounds which exhibit developing properties, but only to show the relation between chemical constitution and developing properties. Little is said about the specific photographic properties of the developing agents. These depend largely, as mentioned on page 331, upon the conditions of application. Thus, such properties can be attributed to the agents themselves only under certain standard conditions, and various standards would be required because some developing agents do not work under circumstances which are necessary for others. No such *general* systematic investigation is known to the author, and the data for the more important developing agents which are available are given in Chapter XI.

Owing to the *flexibility* of the developing agents, fortunately, it is possible to obtain a great variety of results with a few compounds. Thus, the abundance of developing agents only increases the number of ways in which identical effects can be attained. Andresen[91] answers in the negative the question whether the abundance of developing agents is necessary or even desirable for practical photography.

The developers commonly used in practical photography at the present time are almost always compounded with methyl *p*-aminophenol (metol)* and hydroquinone. The success of this mixture appears to be due to the fact that its photographic properties are superior to those of the components taken separately and not just equal to their sum or arithmetic mean. Thus, von Hübl[92] tested three developers, each containing in a liter, 20 grams of sodium carbonate and 60 grams of crystalline sulfite. As the developing agent, he used in one developer 5 grams of hydroquinone; in a second, 5 grams of metol; and in the third, 5 grams of hydroquinone and 5 grams of metol. He found that with the third developer, the velocity of development, using the mixture of the two developers, was greater than the sum of the velocities of development in the metol and hydroquinone developers taken separately. This result was confirmed by Shiberstoff,[93] who made an extensive study of complex developers and especially of the metol-hydroquinone developer. Shiberstoff concludes that the active developing agent in solutions containing metol and hydroquinone is a complex. This complex was isolated and placed on the market by A. and L. Lumière in 1903 under the name *metoquinone;* it contains two molecules of metol associated with one molecule of hydroquinone. Other complex developers of this type mentioned by Shiberstoff are the compound of *p*-aminophenol with hydroquinone, which has been marketed under the name of *pyramidol,* and a compound of hydroquinone with *p*-phenylenediamine. Shiberstoff suggests that the formation of these complex developers can be interpreted as a process of associated salt formation since the two substances may be considered to have different degrees of basicity, the basic amino group of the metol associating with the active hydroxyl groups of the hydroquinone. This complex formation appears to be an association through hydrogen bonds, of which many instances have been found in recent years, although it would be surprising if the complex was present in considerable amounts in the strongly alkaline, dilute developer solutions. Nevertheless, the photographic properties of the mixed developer appear to differ markedly from those of the individual metol and hydroquinone developers. Shiberstoff's results show that even a change in the relative quantities of the metol and hydroquinone contained in the solution does not alter the photographic properties of the developer, since these properties correspond closely to the metoquinone content. He found that the concentration of the developing agent in a metol-hydroquinone developer could be varied without influencing the photographic properties of the developer up to a certain limit, after which the velocity of development as well as the other properties of the developer would begin to change. This limit of concentration he termed the "threshold of active concentration." These results are interpreted by Shiberstoff on the basis of the adsorption theory of development (Chapter VIII, p. 315).

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* This compound is known in photography by a number of trade names, especially *metol*, the original German trade name, and *elon*, the name used by the Eastman Kodak Company.

If the adsorption of the developing agent to the silver bromide grain is considered, it is seen that development is conditioned by the degree of adsorption, which has a definite limit, corresponding to the limiting degree with which the grains can be covered with molecules of the developing agent. This limit depends, of course, upon the intensity of the attraction between the silver halide and the ions of the developer, and Shiberstoff concludes that although it is improbable that a metoquinone complex can exist in an alkaline solution, it is quite possible that this complex is formed in the adsorbed layer on the solid phase. The limiting degree of adsorption for the case of metoquinone is reached at a relatively low concentration of the developer in the solution, and, thus, a small number of molecules of metoquinone in solution would be sufficient to reach the limiting degree of adsorption at which the photographic properties of the developer acquire their constant value. It is seen that the properties of such complex developers are still very obscure and require further work done on them.

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CHAPTER X

THE REACTIONS OF DEVELOPMENT

The chemical reactions which occur in a developing solution during the reduction of silver halide to metallic silver are complicated and not very well understood. The solution itself contains a number of components, all of which may play some part in the reaction. In addition to the developing agent, it contains alkali and sulfite, while bromide is usually added from the beginning and, in any case, is formed during the reaction.

Also, the solution is exposed to air, which produces a direct oxidation of the developing agent, the so-called *autoxidation*, and not infrequently the oxidation product affects the course of the reaction. In some cases, the oxidation products act as catalysts for the primary reactions. In other cases, the oxidized developing agents convert silver back to the ion and arrest the progress of development, even destroying the latent image.

The chemical reactions of development with the metal-containing developing agents are relatively simple and well understood. The metal "increases its valency," *i.e.*, the metal ions are oxidized, losing one or more electrons, the addition of which reduces the silver ions to atoms. The most important of this type of developers are certain solutions containing ferrous salts. The oxidized metal ions are made innocuous, for instance, in the case of ferric ion, by complex formation. In other cases, attempts have been made to reduce the metal ions to the lower oxidized state while development was proceeding and thus to regenerate the developer. Whether or not the solution of an oxidizable metal salt is a developer may depend on the possibility of disposing of the oxidized ions, and a more detailed discussion of their fate is therefore included in the chapter on the developing agents (p. 332).

For the developing agents which do not contain metals, it has been suggested that their capacity to develop the latent image is related to the formation of certain quinonoid oxidation products. These products may determine whether a substance is a developing agent, and this aspect of the reactions of development is discussed in the previous chapter.

While in most developers containing a metal with variable valency the reduced and the oxidized forms differ by only one electron, the non-metal-containing inorganic developing agents and the organic developing agents must lose two hydrogen atoms, *i.e.*, two hydrogen ions and two electrons, to reach another stable state. Configurations with odd numbers of electrons are unstable in these compounds. This probably has some bearing on the above-mentioned influence of the oxidation products of organic developing agents on their activity. If the oxidation products with the reductants form unstable and highly reactive products in intermediary oxidation states, they may catalyze the reducing action of the developing agents. In some instances, intermediates formed by the loss of one proton and one electron may dimerize or may disproportionate to the stable products, *i.e.*, they may split into the higher and lower oxidation products.

The reactions of metal-free inorganic developing agents may be illustrated by the following examples:

Sodium hydrosulfite in development forms bisulfite, according to equation (1):

$$Na_2S_2O_4 + 2AgBr + 2H_2O \rightarrow 2Ag + 2NaHSO_3 + 2HBr.^1 \qquad (1)$$

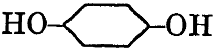
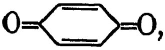
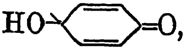
Nothing is known concerning the kinetics and the mechanism of this reaction. The solutions absorb atmospheric oxygen rapidly in a reaction which seems to be catalyzed by silver particles.

The prototypes of the most important organic developing agents, hydroquinone, *p*-aminophenol, and *p*-phenylenediamine, *viz.*, hydrogen peroxide, hydroxylamine, and hydrazine, deserve special notice. Hydrogen peroxide develops only in alkaline solution and does not even reduce a neutral solution of silver nitrate. The reductant proper is obviously an anion. Sheppard and Mees found that one mol of hydrogen peroxide reduces one gram atom of silver to the metallic state and that the gas evolved contains hydrogen. They suggested the reactions:

$$\begin{array}{c} HO{-}O^- + Ag^+ \rightarrow HO{-}O + Ag \\ 2HO_2 \rightarrow H_2 + 2O_2 \\ \hline 2HO_2^- + 2Ag^+ \rightarrow 2Ag + 2O_2 + H_2, \end{array}$$

which are accompanied by

$$O_2^{--} + 2Ag^+ \rightarrow O_2 + 2Ag$$

and by the decomposition of hydrogen peroxide to oxygen and water under the catalytic action of silver. Later investigations, however, have shown that the radical HO_2 is a chain carrier in the decomposition of hydrogen peroxide.[2] It is interesting to note how far the analogy between HOOH and  extends. O=O corresponds to , which is formed by the oxidation of hydroquinone (p. 378) and even HOO— to , which is an important intermediate in this process. However, O_2 and H_2O_2 or their ions do not react with each other as hydroquinone and quinone do.

According to Sheppard and Mees, one mol of hydroxylamine in alkaline solution reduces one ion of silver in development, liberating free nitrogen gas, which produces bubbles in the emulsion. The activity of the developer increases with the concentration of alkali. Investigations by the same authors and by Nichols[3] of the reduction of precipitated silver bromide without binding agent further established that with an excess of hydroxylamine at high alkalinity, a mixture of nitrogen and nitrous oxide is formed. The equations

$$\begin{aligned} H_2NOH + OH^- &\rightleftharpoons H_2NO^- + H_2O \\ H_2NO^- + Ag^+ &\rightarrow Ag + H_2NO \\ 2H_2NO &\rightarrow 2H_2O + N_2 \end{aligned}$$

appear to be more than merely a formal representation of the process, while a plausible explanation for the formation of nitrous oxide has not yet been found. The reaction of hydroxylamine with ammoniacal silver nitrate gives pure nitrogen; that with an alkaline silver salt solution in the presence of sodium sulfite gives a mixture of nitrous oxide and nitrogen. Sheppard and Mees observed that the reaction of hydroxylamine with silver ion in solution is catalyzed by finely divided silver. James[4] studied this reaction under conditions where only nitrogen was formed and found that silver ion and H_2NO^- are adsorbed to the silver surface. This silver catalysis in the reduction of silver ion in solution has an immediate bearing on the theory of physical development and shows that in a physical developer made with hydroxylamine (p. 322), a latent image, consisting of silver, and the growing image catalyze the reduction of silver ion to silver.

Hydrazine, $H_2N—NH_2$, reacts with silver ion according to the equation[5]

$$4Ag^+ + N_2H_4 \rightarrow 4Ag + N_2 + 4H^+.$$

For the organic homologues of the above-mentioned compounds, the literature contains data on the reactions of hydroxylamines and hydrazines. It has been suggested that phenylhydroxylamine[6] in development oxidizes to nitrosobenzene:

$$C_6H_5NHOH + 2Ag^+ \rightarrow C_6H_5NO + 2Ag + 2H^+.$$

When phenylhydrazine was used as a developing agent, benzene was formed as a reaction product.[7] The reaction is probably

$$ArNHNH_2 + 2Ag^+ \rightarrow ArH + 2Ag + N_2 + 2H^+.$$

However, with hydrazobenzene, it is likely that the reaction follows the equation:

$$\begin{aligned} &C_6H_5—NH—NH—C_6H_5 + 2Ag^+ \\ &\qquad \rightarrow C_6H_5—N{=}N—C_6H_5 + 2Ag + 2H^+ \end{aligned}$$

on account of the stability of the azobenzene so formed.

In the study of the reactions occurring in development, much information can be obtained from the autoxidation reactions. The aerial oxidation of the chief representative of the "split" hydrogen peroxide developing agents, hydroquinone, has been the subject of numerous investigations. This substance is rather stable in acidic and neutral solutions but readily absorbs oxygen in alkaline solution at a rate which, below the pK_1 value of hydroquinone,* is proportional to the square of the hydroxyl-ion concentration.[8,9] Under these conditions, hydroquinone forms humic acids of the formula: $((C_6H_4O_3)_x$.[10] In the presence of sulfite, hydroquinone sulfonates result.[11] According to some authors, the first step in these reactions is the formation of quinone and hydrogen peroxide:[12]

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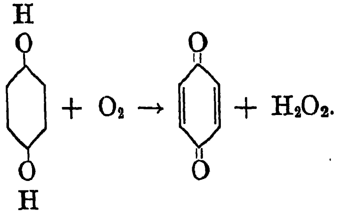
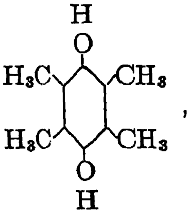
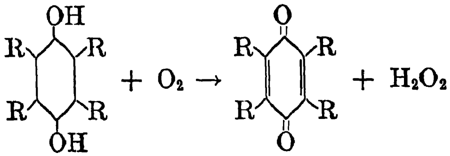
* v. p. 391.



Other authors have suggested hydroquinone peroxide[13] and hydroxyquinone[9] as being the primary oxidation products. The high reactivity of the primary products obviously causes complications which are difficult to disentangle without more definite knowledge of the fundamental processes involved. Therefore, tetramethylhydroquinone, durohydroquinone,

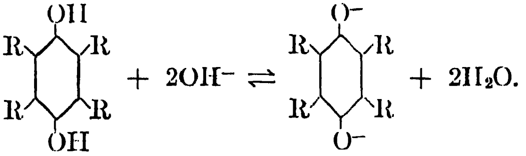


was studied by James and Weissberger.[14] In this hydroquinone, the four nuclear hydrogens, which are very reactive in the benzoquinone, are replaced by the inert $-CH_3$ groups. It was shown that durohydroquinone absorbs molecular oxygen in alkaline solution, with quantitative formation of duroquinone and hydrogen peroxide, both of which can be determined by common analytical processes:



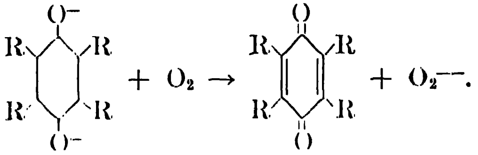
(where $R = CH_3$). (2)

The rate of this reaction is proportional to the square of the hydroxyl-ion concentration. This shows that the first step in the reaction is the formation of the doubly charged durohydroquinone anion:



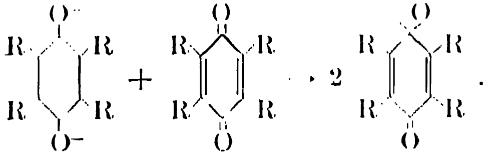
The reaction then splits into two processes:

1. The ion can interact with oxygen in a reaction the rate of which is proportional to the oxygen concentration and the concentration of the durohydroquinone:



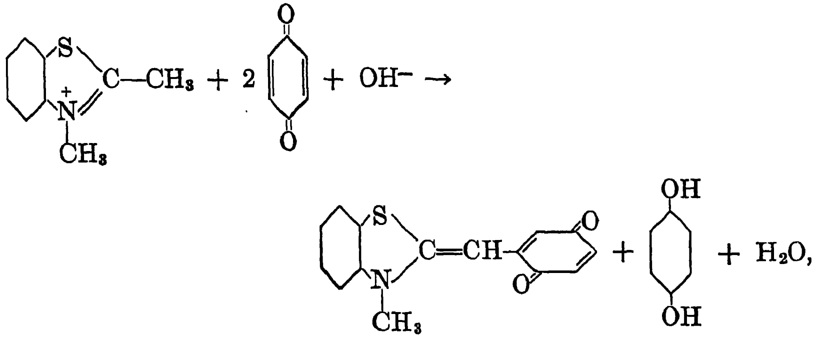
(1)

2. The observation that duroquinone accelerates the absorption of oxygen by durohydroquinone suggests a further path of the reaction. The rate of this process is proportional to the concentrations of the durohydroquinone and the duroquinone, and it is independent of the oxygen concentration. The rate-controlling phase of this reaction must, therefore, be independent of the oxygen and probably consists in the interaction of the durohydroquinone ion with duroquinone. This leads to the formation of a charged radical, a semiquinone, which reacts with oxygen at a high rate:

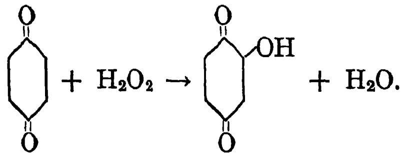


(2)

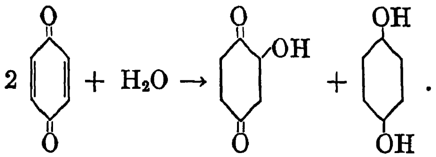
To apply these results to the autoxidation of hydroquinone itself, the autoxidation of the intermediate members of the homologous series was also investigated, $-\text{CH}_3$ groups being gradually replaced by $-\text{H}$.[15] In every case, the reaction proceeded according to (2), where R now stands for CH_3 or H. This was proved with the tri- and dimethylhydroquinones by isolation and identification of the reaction products by common methods. With hydroquinone itself, 2-methylbenzo-thiazole-metho-*p*-toluenesulfonate was added to the reaction mixture. This readily forms a dye with *p*-benzoquinone, according to the equation



and the presence of the quinone can be shown by a spectroscopic analysis of the reaction mixture. When the quinone was quickly eliminated in this way, hydrogen peroxide could be found analytically in amounts which justify the equation (2), R = H. If the quinone is not disposed of, it reacts with hydrogen peroxide in the alkaline solution and forms hydroxyquinone:



Polymerization of the hydroxyquinone eventually leads to the formation of humic acids. Another reaction of the quinone which takes place in the alkaline solution is its disproportionation:[13a,16]



A further disproportionation of the hydroxyquinonate yields the red-brown dihydroxyquinonate ion.[17] The hydroxyquinonate is green; the quinonate, yellow; and the hydroquinonate, colorless.

The rate of autoxidation of hydroquinone and its homologues increases approximately as the square of the hydroxyl-ion concentration, which shows that the oxidation involves chiefly the doubly charged colorless hydroquinone anion.[8,9,18] A slight deviation from the second power may be due to a comparatively slow oxidation of the monovalent ion, which is also suggested by the autoxidation of monomethyl ethers of hydroquinone and of durohydroquinone.

The oxidation of trimethylhydroquinone, as of durohydroquinone, is strongly catalyzed by small amounts of quinone. However, with the trimethylhydroquinone this catalysis reaches a maximum value, above which a further addition of quinone has no effect.[18,19] With small amounts of quinone, when it acts as a catalyst, the autoxidation rate of trimethylhydroquinone is independent of the oxygen concentration, again in analogy to the behavior of the durohydroquinone. As the quinone catalysis reaches its maximum, the reaction rate becomes almost proportional to the oxygen concentration. This variation in reaction may be explained by the formation of an addition compound between semiquinone and quinone. In the region of higher quinone concentrations, the reaction is analogous to the oxidation of hydroquinone, toluhydroquinone, and the xylohydroquinones, the rates of which vary directly with the concentrations of oxygen. No catalysis by quinone has been observed in the autoxidation of the last-mentioned compounds. However, since their autoxidation behaves in all respects in the same way as that of trimethylhydroquinone at the maximum of the quinone catalysis, the experimental results justify the assumption that the autoxidation of the lower members of the hydroquinone series is catalyzed by quinone and that the maximum value of this catalysis is reached at quinone concentrations low enough to escape detection. This assumption is supported by the observation that the addition of stannous salts,[20] of ascorbic acid,* and of some other substances [21] to a solution of hydroquinone lowers the autoxidation rate of the latter. Stannous salts and ascorbic acid eliminate quinone by reducing it to hydroquinone, and these reactions are obviously fast enough to lower the concentration of quinone below the level at which the quinone catalysis reaches its maximum value. The other inhibitors are, likewise, substances capable of reacting with quinone.[22]

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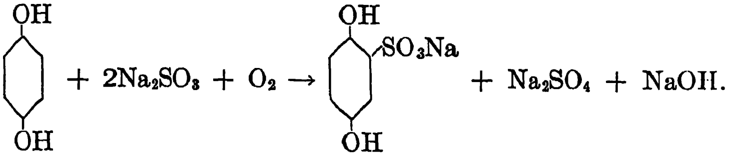
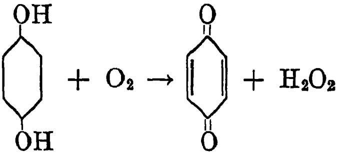
* D. S. Thomas and A. Weissberger, private communication.

A similar mechanism may explain the preservative action of sulfite on hydroquinone. This was first observed by Berkeley.[23] It was attributed by Luther to the oxidation of the sulfite, which prevented oxidation of the organic matter by removing oxygen from the solution.[24] This explanation, however, was not supported by further experiments, which showed that the rate of absorption of oxygen by a solution containing both hydroquinone and sulfite is much lower than that by sulfite alone. Hydroquinone and sulfite mutually inhibit their autoxidation. The inhibitory action of hydroquinone on the autoxidation of sulfite is not discussed here. To explain the action of sulfite on hydroquinone, Pinnow [25] discussed and then abandoned the idea that the sulfite removes traces of copper which catalyze the autoxidation of hydroquinone. Reinders and Dingemans [26] considered the action of sulfite as a chain breaker but rejected the chain mechanism for the autoxidation of hydroquinone.

When hydroquinone undergoes autoxidation in the presence of excess sodium sulfite, according to Pinnow, and Lehmann and Tausch, in the early stages of the reaction, approximately two mols of sulfite are used for every mol of hydroquinone oxidized; one mol of sulfate and one mol of free alkali are formed; and sodium hydroquinone monosulfonate can be isolated from the solution (see (4)). It has been suggested that the hydroquinone monosulfonate is formed from quinone and sulfite (6), and, on the evidence that in the absence of sulfite the first oxidation products of hydroquinone are quinone and hydrogen peroxide, (3) is very probably a composite of (4), (5), and (6). As the

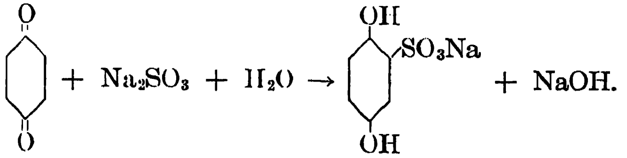


(3)



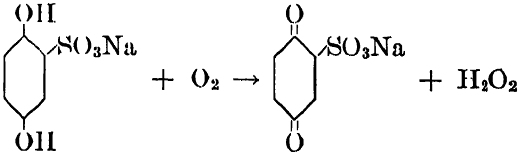
(4)

$$H_2O_2 + Na_2SO_3 \rightarrow Na_2SO_4 + H_2O \qquad (5)$$

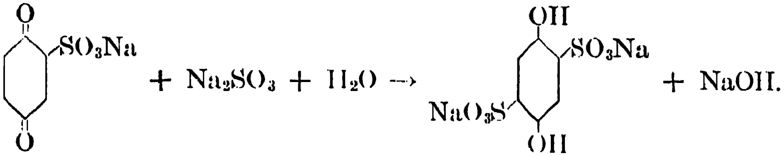


(6)

oxidation proceeds, sodium hydroquinone disulfonate is formed, presumably from the oxidation of the monosulfonate and the reaction of the quinone with sulfite, (7) and (8). All compounds



(7)



(8)

involved in equation (3), except the sodium hydroquinone monosulfonate, of which no satisfactory determination has been made, are formed or consumed in quantitative agreement with the equation, when sufficient sulfite is present and when the solution is made alkaline by sodium carbonate.[13a] According to Mees and Sheppard,[27] dithionate is also formed in the reaction between quinone and sulfite. Toluhydroquinone also forms a disulfonate, whereas the xylohydroquinones and trimethylhydroquinone form only the monosulfonates.

Table XXIII illustrates the extent to which sulfite inhibits the autoxidation of hydroquinone and its homologues. The autoxidation of durohydroquinone is not influenced by the presence of sulfite. These results are in agreement with the assumption that the inhibitory effect of sulfite is due to the elimination of quinone. With durohydroquinone, no reaction of type (6) can take place, and sulfite therefore has no effect on the autoxidation rate of this compound. It may be recalled that other substances which react with the quinone at a sufficient rate also inhibit the aerial oxidation of hydroquinone, *e.g.*, cysteine,[21,22] stannous salts,[20] and ascorbic acid.

An important consequence of the aerial oxidation of developers is the increase in their alkalinity according to (6) and (8).

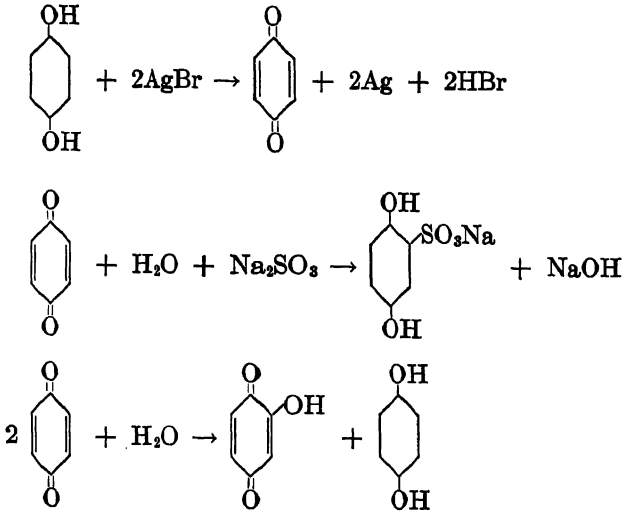
The oxidation of hydroquinone by silver bromide takes a course similar to the autoxidation and produces quinone. With a sulfite-containing alkaline solution of hydroquinone, the following reactions take place.[13a,28] Their summation shows that free

TABLE XXIII

RATE OF AUTOXIDATION OF HYDROQUINONE AND ITS HOMOLOGUES WITH AND WITHOUT SULFITE

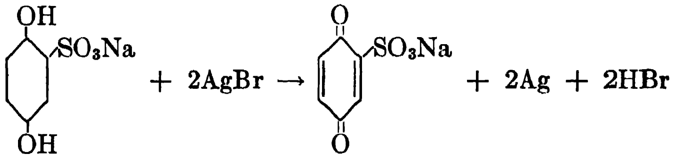
Reaction Volume, 50 ml.; Temperature, 20.0° C. ± 0.02°

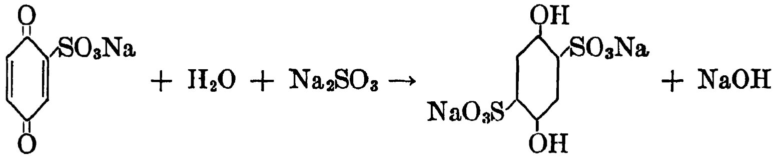
Oxidant	*Amt. of Oxidant in mmol*	*Amt. of Sulfite in mmol*	*Rate of Oxygen Absorption as Rate Constant*
Hydroquinone	½	0	0.0216
		½	.0036
o-Xylohydroquinone	¼	0	0.024
		¼	.0038
m-Xylohydroquinone	½	0	0.045
		½	.014
		¼	.0172
p-Xylohydroquinone	¼	0	0.042
		¼	.0117
			in ml. O_2 *per min.*
ψ-Cumohydroquinone	¼	0	0.90 (max.)
		¼	.125



acid is formed. The alkali added to the developer to maintain the pH at which enough of the developing agent is present in its active form is required to neutralize that acid.

Hydroquinone monosulfonate itself is a developing agent, although a rather weak one, and the reactions



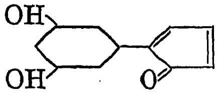


slowly follow those formulated above.

The autoxidation of catechol was studied by Joslyn and Branch.[29] The formation of a very unstable *o*-quinone is assumed to be the first step of the reaction, and the dependence of the reaction rate on the pH shows that at pH values of 6.5 to 10.0, the monovalent ion is the reactive species. At lower and higher pH values, the undissociated molecules and the divalent ions, respectively, react to an appreciable extent. The formation of hydrogen peroxide was demonstrated in the autoxidation of tetrachlorocatechol, in which at a high pH the divalent ion is the active species.[30] The autoxidation of the α-hydroxyketones, on the other hand, proceeds in alkaline solution at a rate linearly proportional to the hydroxyl-ion concentration. The reaction of this $—CO^-{=}COH—$ system was shown to yield the corresponding —CO—CO— compounds and hydrogen peroxide,[31] and formation of hydrogen peroxide is therefore probable also with catechol.

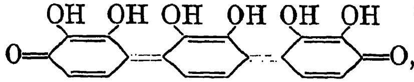
The *o*-quinone with the system —CO—CO— is assumed to be the first step also in the oxidation of catechol with silver bromide, though its instability and polymerization to humic acids[29,32] prevent its isolation. The formation of catechol mono- and di-sulfonates, which are found as the reaction products in sulfite-containing solutions,[28] is explained analogously to equations (6) and (8) (p. 383).

The alkaline solution of pyrogallol is used in gas analysis to absorb molecular oxygen because of the great rapidity of this reaction. The solutions immediately turn dark upon exposure to air, and from the host of oxidation and polymerization products,[10,33] purpurogalline,



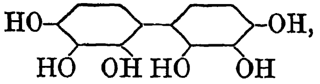
,[34]

and hexahydroxytriphenoquinone,



[35]

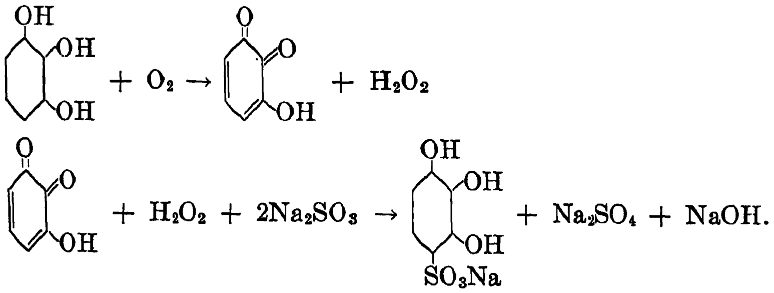
have been isolated. When barium hydroxide is used as an alkali, hexahydroxydiphenyl,



[31]

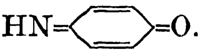
and barium peroxide are found.

The addition of sulfite to the pyrogallol solution again slows down the autoxidation considerably and leads to different reaction products.[30] The oxidation of pyrogallol-containing developing solutions by silver bromide with exclusion of atmospheric oxygen, according to Seyewetz and Szymson,[32,36] yields pyrogallol monosulfonate:



The monosulfonate formed is such a feeble developing agent that it is not appreciably oxidized further, so that the disulfonate has not been isolated from the solution.

Information concerning the hydroxyamino compounds and the diamino compounds is much less complete than that on the dihydroxy compounds.

It has been suggested that the primary product of the aerial oxidation of *p*-aminophenol is quinoneimine, .[32] A polymer of this compound was isolated from the autoxidation products of *p*-aminophenol.[37] The autoxidation of methyl *p*-aminophenol was investigated by Reinders and Dingemans.[38] At a pH between 6.0 and 6.6, the reaction rate is approximately proportional to the hydroxyl-ion concentration and to the concentrations of the methylaminophenol and the oxygen. As a mechanism, these authors suggest that the monovalent negative ion forms a peroxide which goes over into hydroxy-*N*-methylquinoneimine:

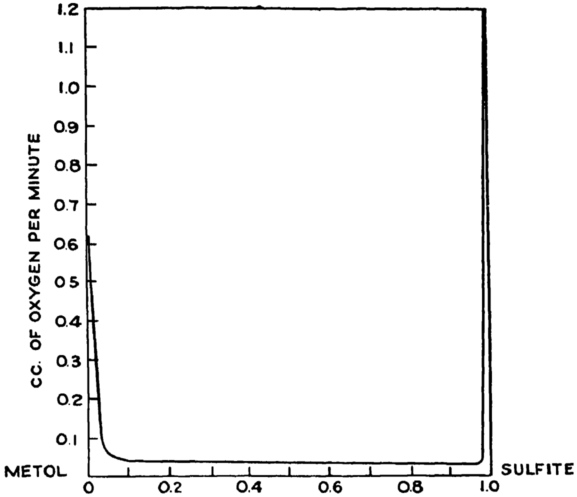


FIG. 104. Mutual influence of sulfite and metol on their autoxidation.

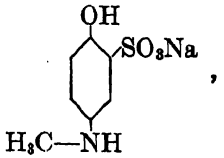
$$
\begin{aligned}
CH_3NH\cdot C_6H_4OH &= CH_3NH\cdot C_6H_4O^- + H^+ \\
CH_3NH\cdot C_6H_4O \quad + O_2 &= CH_3NH\cdot C_6H_4O_3 \\
CH_3NH\cdot C_6H_4O_3 \quad + H^+ &= CH_3N : C_6H_4O_2 + H_2O
\end{aligned}
$$

$$
CH_3NH\cdot C_6H_4OH + O_2 = CH_3N : C_6H_4O_2 + H_2O.
$$

The hydroxyquinoneimine then polymerizes to a nitrogenous humic acid. In analogy to the results with the hydroxy compounds, the primary formation of the methylquinoneimine and of hydrogen peroxide might be considered likely.

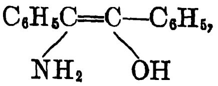
Sulfite acts as a strong antoxidant on *p*-aminophenol and on methyl *p*-aminophenol. The effect on the autoxidation of the latter compound and of the methyl *p*-aminophenol on the aerial oxidation of sulfite is shown by the diagram (Figure 104).

According to Seyewetz and Szymson[32] and Lehmann and Tausch,[13a] the oxidation of *p*-aminophenol by silver bromide in sulfite-containing solutions yields *p*-aminophenol monosulfonate, which does not react further in carbonate-alkaline solution. However, in caustic solution, it develops very slowly, and the reaction proceeds to the disulfonate. Methyl *p*-aminophenol, on the other hand, even in carbonate-alkaline solution, readily forms not only the 4-methylaminophenol-2-sulfonate,



but also the disulfonate. According to Lehmann and Tausch,[13a] the monosulfonation deprives methyl *p*-aminophenol of its developing energy to a smaller extent than hydroquinone.

An aqueous solution of *o*-aminophenol reacts with oxygen to form complex condensation products from which aminophenoxazon was isolated.[39] No kinetic study has been made. However, the autoxidation of desylamine, $C_6H_5CHNH_2COC_6H_5$, which in its tautomeric form,



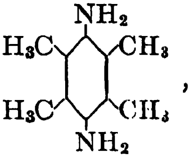
$$\underset{NH_2}{C_6H_5C}{=}\underset{OH}{C}{-}C_6H_5,$$

is the analogue of *o*-aminophenol, proceeds with the formation of hydrogen peroxide, ammonia, and benzil, $C_6H_5COCOC_6H_5$, the negative ion being the reactive species.[40]

When oxidized with silver bromide in carbonate-alkaline sulfite-containing solutions, *o*-aminophenol forms the monosulfonate; in caustic solution, it yields the disulfonate.[32,36]

Diaminophenol, when oxidized with silver bromide in sulfite solution, gives the disulfonate even without additional alkali. The 2-amino-1-naphthol-6-sulfonate in carbonate-alkaline sulfite solution is oxidized to the 2-amino-1-naphthol di- and trisulfonates.

p-Phenylenediamine autoxidizes in alkaline solutions with the formation of quinonediimine. The aerial oxidation of diaminodurene,



appears to reach a maximum rate at a pH of about 8. This value does not appreciably change when the pH is increased to about 11. The free base is obviously the reactive species. The autoxidation proceeds with elimination of ammonia, and the product formed is duroquinone. The latter catalyzes the reaction in a manner similar to that described for durohydroquinone. This denitrogenation is similar to the elimination of ammonia in the autoxidation of α-amino ketones.

In the presence of sulfite, *p*-phenylenediamine yields *p*-phenylenediamine sulfonate, and the same reaction takes place if the oxidizing agent is silver bromide. In carbonate-alkaline solution, it stops with the monosulfonate; however, in caustic solution the reaction proceeds to the disulfonate.[32]

p-Hydroxyphenylglycine in sulfite-containing solution forms the monosulfonate, which even in caustic alkaline solutions is not a developing agent.[32]

It is evident from the foregoing that not only the rate of action of a developing agent but also the maximal amount of silver ion which it reduces to silver depends on the conditions of the solution. A number of investigations have been made to determine the "reducing power" of developing agents; *i.e.*, the amount of silver in solution or of precipitated silver bromide which these developing agents reduce to silver under various conditions.[32,41]

The investigations of Sheppard and Mees on hydrogen peroxide and hydroxylamine as developers and those of Seyewetz and Szymson are discussed in Chapter VIII. From the results of the latter, it follows that for all practical purposes hydroquinone, pyrogallol, *p*-aminophenol, glycine, and *p*-phenylenediamine in sulfite-containing carbonate-alkaline solutions reduce two silver ions per unit of developing agent. In caustic alkali, the monosulfonates of metol and *p*-phenylenediamine may act strongly enough as developing agents to increase significantly the reduction equivalent of the parent substances. According to T. H. James,* metol-monosulfonate may participate substantially in development, even in carbonate solution.

Earlier, Andresen,[41c] working with precipitated silver bromide, gave the following figures:

TABLE XXIV

REDUCTION EQUIVALENTS OF SOME DEVELOPERS CONTAINING SULFITE

Developing Agent	*Mol AgBr Reduced*
Hydroquinone	4.4
Catechol	1.9
o-Aminophenol	0.7
N-Methyl-*o*-aminophenol	1.0
p-Aminophenol	3.9

In a solution not containing sulfite, one mol of *p*-aminophenol reduced only 1.2 mols of silver bromide. The developers in Table XXIV contained sulfite and the type of alkali commonly used with the developing agent in question, for instance, caustic alkali with *p*-phenylenediamine and carbonate with hydroquinone. The alkali concentrations are stated to be the usual ones but are not specified further.

Bogisch,[41d] in a similar investigation, found that 1.4 grams of hydroquinone in a developer containing 20 grams of carbonate and 20 grams of sulfite in 150 cc. of water in one hour reduces 5.9 mols of silver bromide per mol of hydroquinone. At a higher dilution (300 cc.) and at shorter times (½ hour), this amount drops to about 4.3 and 5.3, respectively. With silver chloride as oxidant, the reduction equivalent reaches almost 8. This value is also obtained with a sulfite-containing ammoniacal silver nitrate solution and indicates the formation of quinonetrisulfonate as oxidation product, while in practical development mainly hydroquinone-monosulfonate is formed.

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* Private communication.

The alkali regulates the activity of the developer through the influence of the pH on the concentration of the active species of the developing agent and takes care of the acid which is formed in development. For the latter purpose, not only the initial pH but also the buffering capacity, *i.e.*, the amount of acid which the solution can take care of without changing the pH beyond a certain limit, are of obvious importance. Table XXV shows the pH of solutions used in developers, and Table XXVI, the pK values for some of the developing agents as given by various authors. pK is the negative logarithm of the dissociation constant. Its numerical value gives the pH at which the compound is 50 per cent dissociated.

TABLE XXV

pH VALUES OF DEVELOPER SOLUTIONS*

5–10% solution of sodium carbonate	11.5
1–5% solution of sodium metaborate	10.5–10.8
1–5% solution of sodium tetraborate (Borax)	9.0
5–10% solution of sodium sulfite	9.0

* H. D. Russell, private communication.

TABLE XXVI

pK VALUES OF DEVELOPING AGENTS[29, 42]

	Acid Dissociation pK_1	pK_2	*Basic Dissociation* pK
Hydroquinone	9.8	11.5	
Catechol	9.3		
Pyrogallol	8.8	11.1	
p-Aminophenol	10.3		8.2
Methyl-*p*-aminophenol	10.4		8.0
p-Aminodimethylaniline			7.4

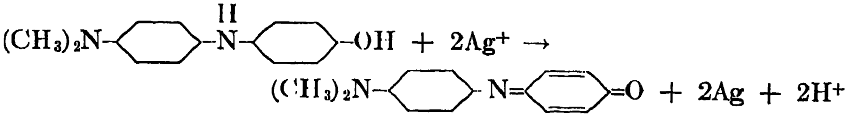
There are various reports in the literature on the specific effects of different types of alkali. The specific effect of borate is confirmed and well understood, being due to the esterification of boric acid with compounds containing neighboring —OH groups. In general, however, the velocity of development changes with the pH of the solution, independently of the nature of the alkali used for securing this pH value.[43]

In addition to the influence of the pH on the concentration of the active species of the developing agent, the alkalinity of the developer in many cases has a further effect. It was mentioned that appreciable amounts of the quinonoid oxidation products of developing agents may interfere with the development process. In the common developers, these products are made innocuous by reaction with sulfite at a rate which is likely to increase with the alkalinity of the solutions.[44] Besides this reaction with the sulfite, the oxidation products undergo many reactions, which were mentioned on various occasions, and their rate increases with the pH.[45] Thus, high pH in a developer further assists the work of the developing agent by eliminating its oxidation products.

In the common practice of development, little attention is paid to the oxidation products of the developing agent as long as they do not stain the gelatin. The preference today is for developing agents and developers with colorless, soluble oxidation products, such as the sulfonates, which are formed in sulfite-containing solutions. With pyrogallol as a developing agent, however, even the presence of sulfite does not totally prevent the formation of dark oxidation products which dye and tan the gelatin. The image consists to an appreciable degree not only of silver but also of the developer oxidation products. These remain when the silver is removed, for instance, by Farmer's reducer, and the image formed by them is called the *residual image*. With hydroquinone, catechol and pyrogallol, in the absence of sulfite, these oxidation products are identical in their reactions with those formed by the autoxidation of the developing agents.[46] However, the formation of peroxide in the autoxidation process would be expected to cause some difference.

With pyrogallol developers, the effect of the stain produced by the oxidation products upon the printing quality of the image is very important. The spectro-selectivity of photographic deposits was studied by Jones and Wilsey.[47] They called the value of $\frac{\gamma_p}{\gamma_v}$ the *color coefficient*, where γ_p is the slope of the straight-line portion of the characteristic curve determined photographically, bromide paper being used as the printing material; and γ_v is the slope as determined visually. Wilsey[48] applied the strong color obtained with the pyrogallol developer as a method of photographic reduction or intensification, the original negative being bleached and then redeveloped in a developer adapted to produce stain (p. 554). The value of the color coefficient depends upon the sulfite content of the developer, the maximum amount of sulfite giving a color coefficient as low as 1.05, while in the absence of sulfite a pyrogallol developer may have a color coefficient of 2.0.

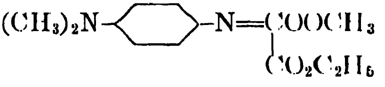
While in black-and-white development the oxidation products are of fundamental importance only in rare cases, for other photographic processes the ability of the oxidation products to tan gelatin and act as mordants for dyes has lent interest to developers which do not contain sulfite or contain only a little.[49] The dye deposits which are formed when compounds like indoxyl, hydroxycarbostyril, thioindoxyl, and the leuco bases of indophenols, indamines, and azophenines are used as developing agents have become the basis of color photographic processes. The equation



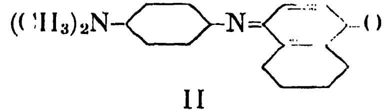
shows a case where one mol of dye is formed for every two silver ions reduced.

Another method of producing colored images is the condensation of the oxidized developer with couplers to form dyes. This was suggested by Fischer and Siegrist.[50] It is the method used for producing the dyes in the Kodachrome multilayer process of color photography.[51] In Fischer's original multilayer process, the couplers were intended to be incorporated in the emulsion layers. Care must be exercised in a multilayer process that each coupler acts only in the layer in which the respective dye deposit is desired.

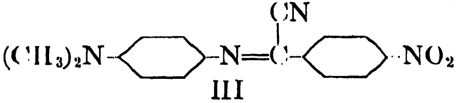
With *p*-aminodimethylaniline as a developing agent, a yellow dye I is obtained with acetoacetic ester; a cyan dye II, with α-naphthol; and a magenta dye III, with *p*-nitrobenzyl cyanide. The formulas give one extreme form only of the resonance systems (Chapter XXIV) of which the dye consists.



I

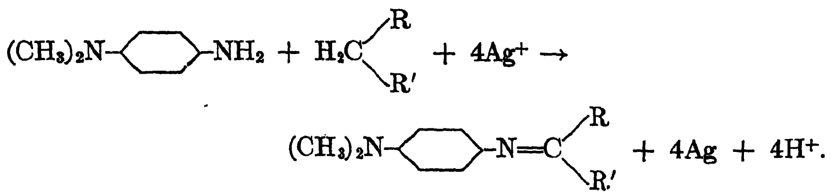


II



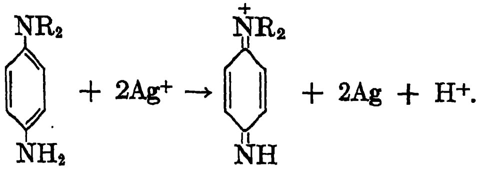
III

The mechanism by which these dyes are formed is still far from being well understood. Summarily, it is represented by the equation[52]



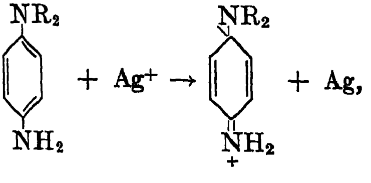
This may be supplemented by the following:*

The oxidation of an unsymmetrical *p*-phenylenediamine in photographic development is most likely to produce a quinonediimine ion



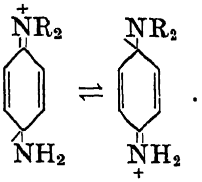
(9)

This reaction can proceed in two steps, *i.e.*, through an intermediate semiquinone ion, which has one less electron than the original developer and is a charged radical,[53]



(10)

which is stabilized by resonance between the forms A and B:



A B

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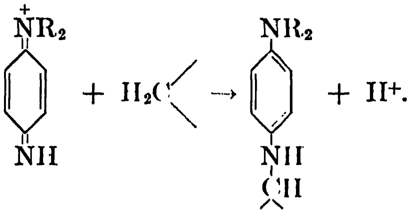
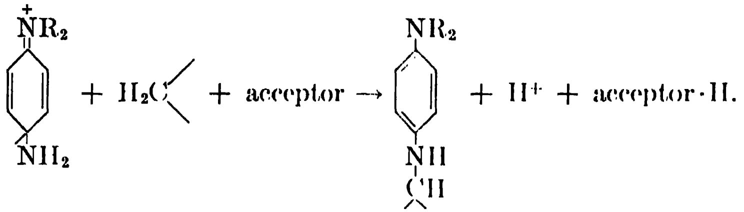
* D. S. Thomas and A. Weissberger, private communication.

The quinonediimine ion may react with a coupler containing an active methylene group, $H_2C<$, to form a leuco base, according to the equation:



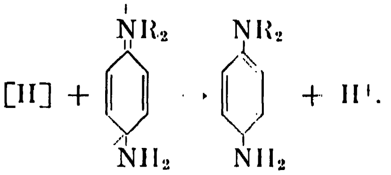
(11)

The semiquinone ion can form this leuco base only in the presence of a hydrogen acceptor, as shown by equation (12):



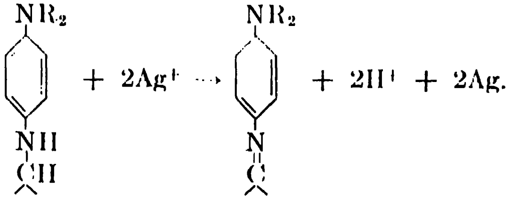
(12)

The acceptor may be a second semiquinone ion which in the reaction regenerates the developing agent (13):



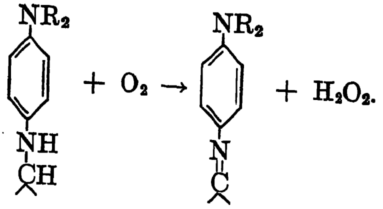
(13)

For the oxidation of the leuco base to the dye, several possibilities may be considered. The leuco base may react as a developer:



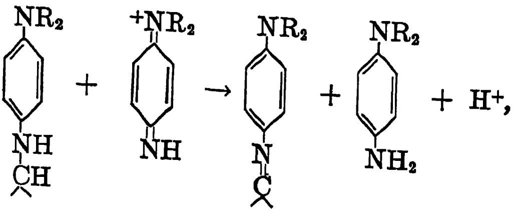
(14)

It may be oxidized by oxygen, probably with the formation of peroxide (15):



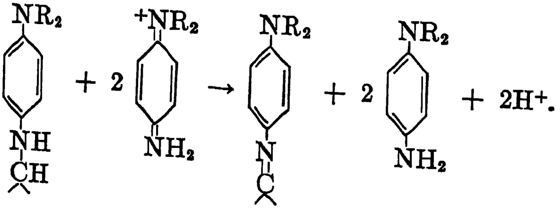
(15)

It may be oxidized by the quinonediimine ion (16):



(16)

or it may be oxidized by the semiquinone ion (17):



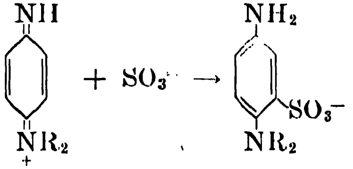
(17)

In a discussion of these possibilities, it is important that the dye deposits are not necessarily restricted to the sites of the individual grains but may be spread out in clouds around them. Inasmuch as the leuco bases and the dyes under consideration do not diffuse in gelatin, both must be formed at the place where the dye is eventually found, *i.e.*, at least partially at some distance from the grains. Hence, the oxidizing agent for the corresponding amount of the leuco base must be mobile, and silver ions must be in solution to act as the oxidizing agent according to (14). A still more striking argument for the mobility of the oxidizing agent is the existence of color processes in which the coupler is incorporated in the emulsion. The bulk of the coupler is located at some distance from the silver halide grains, and it is not very probable, therefore, that the silver ions oxidize the leuco base in these processes.

Some, at least, of the leuco bases in question are easily oxidized by air in alkaline solution. Hence, it is possible that (15) plays some part in color development. The extent to which the oxidation is performed by air depends upon the relative rates of the oxidation reactions and the concentrations of the reactants. Reactions 16 and 17 or both, which have been neglected in the literature, are likely to be of great significance.

In addition to forming a dye, the oxidized developer may polymerize or decompose, or it may react with sulfite. These reactions are familiar in black-and-white development. Some developers of very high pH form dye images contaminated with a brown stain, which has been attributed to polymerized and decomposed oxidation products of the developing agent. However, this can be avoided by a proper choice of developer.

The sulfite reacts readily with the oxidized developer to form sulfonates (18):



(18)

and thus competes strongly with the coupler for the oxidized developer. The final result of this competition, *i.e.*, the relative amounts of dye and sulfonate formed for a given amount of reduced silver, depends on the rates of the various reactions involved and on the concentrations of the reactants at the site of the reaction.

The availability of the oxidized developer in a certain volume element of the emulsion is determined by the rate of development. This, in turn, depends, for a given emulsion, on the concentration of the active species of the developing agent at the silver halide grain and, thus, on the rates of diffusion of the respective components of the developer. Conditions may arise in which the rate of diffusion of the developing agent becomes the limiting factor for the rate of development. For a given concentration of oxidized developing agent, likewise, the formation of sulfonate and of dye in any particular volume element of the emulsion depends upon the concentrations of sulfite and coupler, respectively, in this volume element. If the concentration of oxidized developing agent in this volume element is high, sulfite and coupler may be used up at a rate which lowers their concentrations, and their rates of replacement will become important for the ratio of dye to sulfonate and, therefore, of dye to silver. The diffusion rates of sulfite and coupler may then determine the dye/silver ratio.

In addition to the examples given by Fischer and Siegrist, many developers and couplers providing dyes of suitable absorption characteristics and stability have been disclosed in recent years, chiefly in patents.

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CHAPTER XI

THE KINETICS OF DEVELOPMENT

When an exposed photographic material is placed in a developer, the exposed grains are attacked as the developer penetrates into the layer and are reduced to metallic silver. The mechanism of this attack is discussed in Chapter VIII, and the chemistry of the reaction between the developing solution and the exposed silver halide, in Chapter X. The rate at which the attack proceeds was first investigated by Hurter and Driffield and published in their famous paper in 1890.[1]

Hurter and Driffield adopted as their standard developer ferro-oxalate, which they found convenient and which has the further advantages that the course of its chemical reaction is well understood and that the solution contains no solvent for silver halide (p. 310). They determined experimentally the rate at which the density corresponding to a given exposure grows during development and noted that the density increases rapidly at first, its growth becoming slower as time advances, and finally tends to a limit. This was expressed by a formula "based upon the idea that the number of particles of bromide of silver affected by the light is greatest in the front layer of the film and decreases in geometrical progression as each succeeding layer of the film is reached." This formula is

$$D = D_\infty(1 - a^t),$$

where D_∞ represents the amount of image which is finally developable, D equals the density at time t, and a is a constant. It is seen that this formula is derived from the idea that the developer reduced the exposed particles as it penetrated the film, but a conclusive experimental disapproval of this hypothesis was given by Sheppard and Mees,[2] who showed that a plate exposed from the glass side develops normally although, in this case, the developer reaches first the layer containing the fewest exposed particles. Since the publication of Sheppard and Mees' work, there has appeared a letter to Driffield dated August 22, 1897,[3] in which Hurter wrote that diffusion worked so rapidly that there was no need to assume a limit to development for want of developer or that the bromide generated in the film affected the rate of development since it escaped by diffusion as the developer entered. Hurter pointed out that the diffusion phenomenon, to some extent, affected the results,

> "and these results will naturally deviate in consequence from any simple rule, which cannot be so formulated as to take account of everything—constitution of film, quality of gelatin, velocity of diffusion to and fro, temperature, etc.
>
> "All that mathematical analysis can do is to trace the *main* features of the course of development."

In this, Hurter anticipated the later conclusion of Nietz,[4] that the process of photographic development, including the diffusion factors, is necessarily so complicated that a simple law is unlikely to describe it accurately. However, Hurter proceeds:

> "Let the total quantity of silver on any part of the plate be A. After illumination this consists of two portions, unaffected bromide $= B$ and an affected part a, and always will, $B + a = A$. *The difference between the two portions is not one of kind, but simply one of degree in rapidity of development,* and this thought applied to the density of the resulting image makes that (in imagination) also consist of two parts, *i.e.*, of developed *fog* and developed *image.* Call the one x (image) and y the fog, then the density will be $x + y = D$.
>
> "The small amount of latent image developed at any moment will be, say—dx and that amount is developed in the moment dt, hence the velocity of development is expressed as $\frac{dx\ (\text{image})}{dt\ \ (\text{time})}$.
>
> "This velocity will be proportional to a factor K_1, which depends upon the constitution of the developer, and to the amount of undeveloped latent image present at that moment which we are considering. Let the latent image already developed be x, then $(a - x)$ is the amount of undeveloped latent image and the velocity of development (growth of density in unit time) is
>
> $$\frac{dx}{dt} = K_1(a - x)."$$

This equation integrates into the equation given by Hurter and

Driffield in their paper, but Hurter preferred to express it in the form

$$D = D_\infty(1 - e^{-Kt}),^*$$

which is that adopted by Sheppard and Mees and deduced by them not from any theory as to the distribution of the developable halide but from a consideration of the velocity of reaction in heterogeneous systems, among which the development of silver bromide naturally stands.

The problems of penetration were studied by Sheppard and Mees, who found that when photographic plates were exposed from the glass side, the image would be visible from the back somewhat sooner than on the face for the short exposures in which the greater reactivity of the more exposed particles was the predominant factor, but for the longer exposures, the time required for the developer to penetrate the emulsion enabled the image to appear first on the less reactive but more accessible surface. They concluded that:

> "(*a*) The absolute thickness of the layer of developable particles increases but slightly with the exposure.
>
> "(*b*) Reckoning down through the layer from the exposed side, the reactivity of each layer of grains diminishes through the depth. *The slope* of this reactivity gradient then depends upon the exposure.
>
> "(*c*) The penetration is complete at a very early stage of development, but as the developer reaches the lowest layers, its concentration will be diminished somewhat by diffusion and oxidation by developable AgBr. There will therefore be a concentration gradient through the film.
>
> "(*d*) Then in the case of exposure from the film side, the two gradients will be in the same sense and will reinforce each other; for exposure from the back they will be opposite in direction, and the front layers or the back may appear first according as one factor or the other predominates. This result is in agreement with the microscopic deduction that, *ceteris paribus*, the more exposed grains possess the greater reactivity, and start development first."

An estimate of the absolute time required for the developer to penetrate the thickness of the emulsion showed that this occurred in less than ten seconds, while the half-period of development under these conditions was five minutes. They concluded that the delay in appearance due to diffusion was normally negligible in comparison with chemical effects. A study of the actual invasion of the developer confirmed these results. When a dry film of gelatin is placed in water, the absorption is largely a surface-tension phenomenon, depending upon the capillary structure of the gel, and similar to the wetting of powders. The rate is very rapid at first and then falls off somewhat steeply with the time, the decrease in velocity frequently being exponential, so that if a_∞ is the maximum amount of water absorbable, a the amount at any time t, then

---

* In accordance with present practice, the velocity constant is expressed in this book by k, not K.

$$da/dt = k(a_\infty - a).$$

Dilute solutions of electrolytes are absorbed at much the same rate as water, more concentrated ones less rapidly, while if a plate of gelatin is first soaked in water, then in a salt solution, the latter rapidly displaces the water. They summarized their conclusions as follows:

> "(*a*) A plate soaked in water to near its maximum swelling develops as fast, or faster, than a dry plate.
>
> "(*b*) While the amount absorbed only increases slightly with the concentration, the development velocity is directly proportional to this.
>
> "(*c*) The temperature coefficient of development is generally greater (1.7–2.5) than that of absorption (1.3–1.5).
>
> "(*d*) The viscosity of the solution may be greatly increased without lowering the velocity of development.
>
> "(*e*) Hardening the film lowers the rate of absorption without altering the development velocity."

As is mentioned above, Sheppard and Mees considered the action of the developer on the silver bromide a heterogeneous reaction. When a solid dissolves, the rate is proportional to its surface and to the difference between the saturation-concentration and the concentration at the given moment. At the boundary between the phases, saturation exists, so that the rate of solution depends on the diffusion velocity. When a chemical action is superposed, Nernst assumed that in most cases the equilibrium in the reaction-layer is adjusted with practically infinite velocity compared with the diffusion process (p. 414). If the length of the diffusion path and the diffusion coefficients are known, in many cases the velocity may be calculated in absolute measure.

The chemical equation for development with ferro-oxalate is probably

$$Ag^+ + Fe(C_2O_4)_2'' = \underset{\text{(met.)}}{Ag} + Fe(C_2O_4)_2';$$

that is, one silver ion is converted into metallic silver. The velocity equation will then be $dx/dt = kC_{Ag} \cdot C_{FeOx^-}$.

C_{Ag} may be reckoned as constant on the view given above of the instantaneous adjustment of the equilibrium, since solid silver bromide is present. If it is assumed that diffusion takes place in a layer of constant thickness, δ, there will diffuse into the reaction-layer $S \frac{\Delta}{\delta} (a - x)dt$ of reducer in the time dt, where Δ is the diffusion coefficient of the reducer; a, its initial concentration; and x, the equivalents of AgBr reduced. If x is very small compared with a, the total concentration, this becomes $S \frac{\Delta}{\delta} a \cdot dt$, and the velocity of development is given by $dx/dt = kS$, where S is the surface of the solid phase, and $k = \Delta \cdot a/\delta$. In this equation, S, the surface of the solid phase, represents a quantity of silver halide which is developable because it has been exposed, and in the course of the reaction this varies from the total amount which has been exposed, and which when developed gives the image D_∞, to zero, so that the amount of exposed silver bromide available for development at any time, t, is equal to $(D_\infty - D)$, where D is the density of reduced silver at the time, t.

Therefore, $dD/dt = kS = k(D_\infty - D)$, which gives on integration

$$\frac{1}{t} \ln \frac{D_\infty}{D_\infty - D} = k.$$

If this is written in its exponential form, it is Hurter's equation $D = D_\infty(1 - e^{-kt})$. A satisfactory test of this equation can, as seen later, be made only in the absence of much free bromide and, at the same time, only with a developer and emulsion which do not produce fog on prolonged development, since otherwise D_∞ is not constant; grains which were not exposed become developable as development is prolonged. By using plates which were slow and free from fog, together with the ferro-oxalate developer and low concentrations of bromide, Sheppard and Mees were able to demonstrate the validity of the equation and

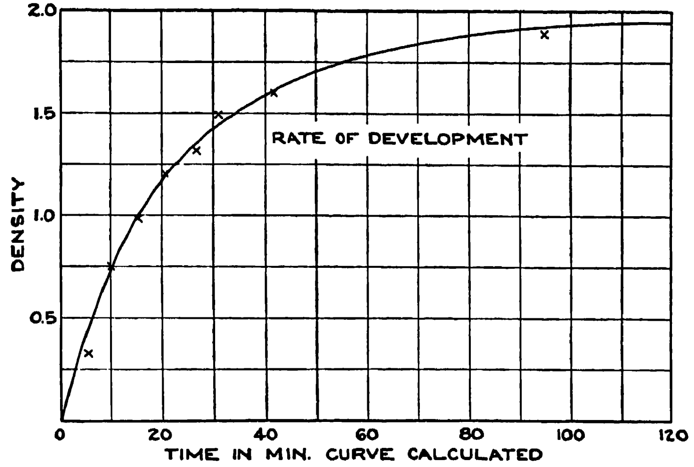


Fig. 105. Growth of density with time of development in ferro-oxalate.

TABLE XXVII

Relation between Density and Time of Development
(Sheppard and Mees)
Developer: N/25 Ferro-Oxalate Containing N/500 KBr

Time	D_1	D_2	D_3	*D average*	*D calc.*
5.0 mins.	0.330	0.303	0.373	0.335	0.410
10.0 "	0.773	0.815	0.697	0.762	0.736
15.0 "	1.013	0.975	1.020	1.003	0.995
20.0 "	1.227	1.232	1.228	1.229	1.201
25.0 "	1.330	1.365	1.296	1.330	1.364
30.0 "	1.510		1.510	1.510	1.495
40.0 "	1.610			1.610	1.681
95.0 "	1.904			1.904	1.960
135.0 "	1.970			1.970	1.980
∞	2.000	2.000		2.000	2.000

so very satisfactorily confirmed the earlier work of Hurter and Driffield. Their results for three experiments repeating each other are given in Table XXVII, together with the average observed values of density and the value of density calculated from the equation. These results are shown in Figure 105.

A deduction from this equation is the law of constant density ratios. If a series of increasing exposures are given to a material which is then developed in a non-fogging developer free from bromide, as the densities corresponding to different exposures increase proportionately, the ratio of the densities due to any two exposures is constant and independent of the time of development. Hurter and Driffield showed that if a geometrically increasing series of exposures are given to a plate, over a certain range the density increases arithmetically.* Over this period, the following equation holds:

$$D = \gamma \log E/i,$$

where E is the exposure, i is a characteristic constant of the plate, termed the *inertia*, and γ is a constant depending upon the development and called the *development factor*. The magnitudes i and γ are obtained graphically as follows: The densities due to nine successive exposures are plotted as ordinates, and the logarithms of the corresponding exposures, as abscissae. A curve is obtained which, for a certain period, is practically a straight line (Figure 68, p. 203). The point where this cuts the exposure axis gives $\log i$, and if θ is the angle of inclination, $\gamma = \tan \theta$. Analytically, the value of γ may be deduced as follows: For two exposures, E_1 and E_2, the densities D_1 and D_2 are obtained, the equations being

$$D_1 = \gamma \log E_1/i, \qquad D_2 = \gamma \log E_2/i.$$

Eliminating i,

$$\gamma = \frac{D_2 - D_1}{\log E_2 - \log E_1}.$$

If a number of strips of film bearing sensitometric exposures are developed for progressively increasing times in a solution containing little or no free bromide, the characteristic curves will have straight-line portions which will meet when projected to a common point on the log E axis. The following table gives an experimental determination of such a set of curves. These curves were made from exposures on supersensitive panchromatic sheet film developed in a solution of the following composition:

---

* This work by Hurter and Driffield is discussed from other points of view in Chapter V, p. 201 and in Chapter XIX, p. 699.

Pyrogallol	5.0	grams	
Sodium Sulfite	37.5	"	
Sodium Bisulfite	4.25	"	
Sodium Carbonate	18.75	"	
Potassium Bromide	0.0595	"	(N/2000)
Water	1.0	liter	

The density values were corrected according to the Meidinger-Wilsey fog-correction formula (Chapter XVII, p. 649).

TABLE XXVIII

DENSITIES FOR VARIOUS TIMES OF DEVELOPMENT

Log E ($M.C.S.$)	*5 minutes*	*8 minutes*	*12 minutes*	*20 minutes*
$\bar{1}.97$	1.39	1.70	2.00	2.26
$\bar{1}.67$	1.18	1.49	1.74	1.97
$\bar{1}.37$	0.96	1.21	1.42	1.60
$\bar{1}.70$	0.74	0.93	1.08	1.23
$\bar{2}.77$	0.54	0.66	0.75	0.85
$\bar{2}.47$	0.35	0.39	0.45	0.51
$\bar{2}.17$	0.19	0.20	0.23	0.25
$\bar{3}.87$	0.07	0.08	0.08	0.09
$\bar{3}.57$	0.01	0.01	0.01	0.01
$\bar{3}.27$	0.00	0.00	0.00	0.00

These data are plotted in Figure 106. It is seen that the straight-line portions of the curves produced meet at the point i on the exposure axis, so that the effect of the continued development is to produce a rotation of the curves around the point i. For the straight-line portions of the exposure curves, $D = \gamma(\log E - \log i)$, and for a single exposure, the expression in brackets is a constant, and γ is therefore strictly proportional to D.

Sheppard and Mees pointed out that since $D = D_\infty(1 - e^{-kt})$, $\gamma = \gamma_\infty(1 - e^{-kt})$, where $\gamma_\infty = \gamma$ at infinite development.[5] The γ, t curve corresponding to Figure 106 is plotted in Figure 107, the calculated value of γ_∞ being 1.28 and of k, 0.170.

The magnitude, γ_∞, that is, the limiting γ of the emulsion, is of great importance. It states numerically the ultimate contrast and quality of the material expressed by such phrases as contrasty, soft, and so forth. γ_∞ is, of course, proportional to the photometric equivalent (Chapter V, p. 226) of the reduced silver, but it is dependent primarily upon the distribution of sensitivity among the grains and, thus, upon the size-distribution curve of the grains themselves. The more uniform the grains are in sensitivity (and consequently in size), the higher will be the value of γ_∞. k, the velocity constant of development, is dependent on a number of factors relating to the developer itself and to the nature of the emulsion. For the same emulsion, it can have any value, according to the developer, and it is notably affected by the temperature. For the same developer, it varies very much with the emulsion, some emulsions developing with a much higher velocity constant than others, even though they may have the same value of γ_∞. As photographic materials are kept, the value of k tends to decrease for some time owing to changes occurring in the gelatin, so that

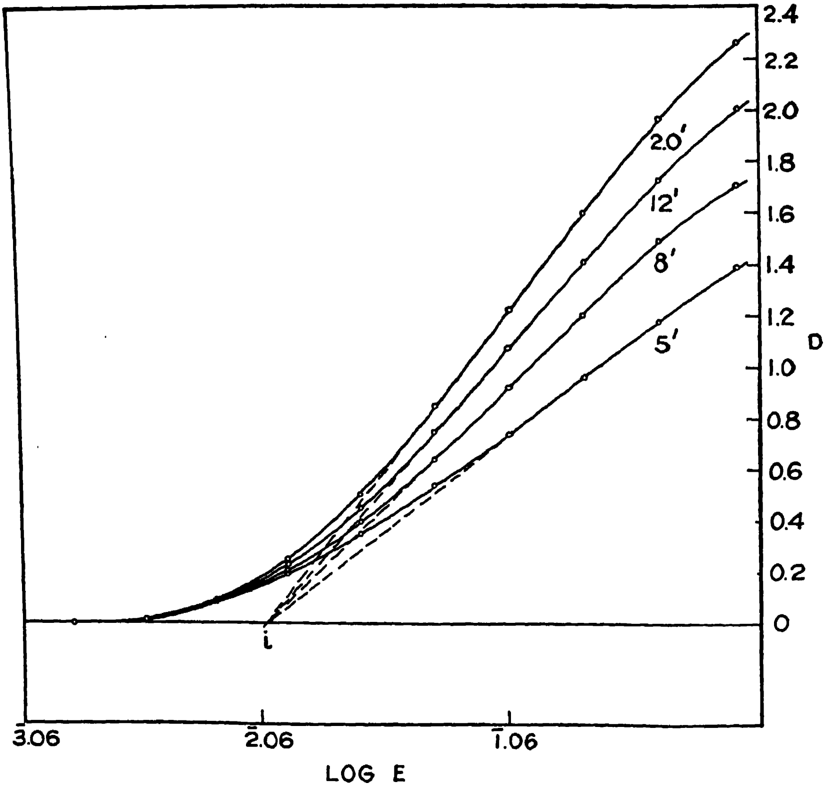


FIG. 106. Change in the characteristic curve with time of development.

while γ_∞ is almost constant during the life of the material, the rate of development tends to decrease somewhat with age owing to a decrease in the value of k.

In practice, it is not easy to determine the value of γ_∞ experimentally since the prolonged development necessary to attain an approximation to γ_∞ tends to produce fog. There is, therefore, a practical limit to the contrast of a given material which can be attained during development, because at a certain value of γ, the increase of fog prevents any further rise. With materials of good quality, however, the practical value obtained is not far removed from the theoretical limit, and since γ_∞ is not greatly affected by the presence of bromide, a bromided developer may be used for its experimental determination.

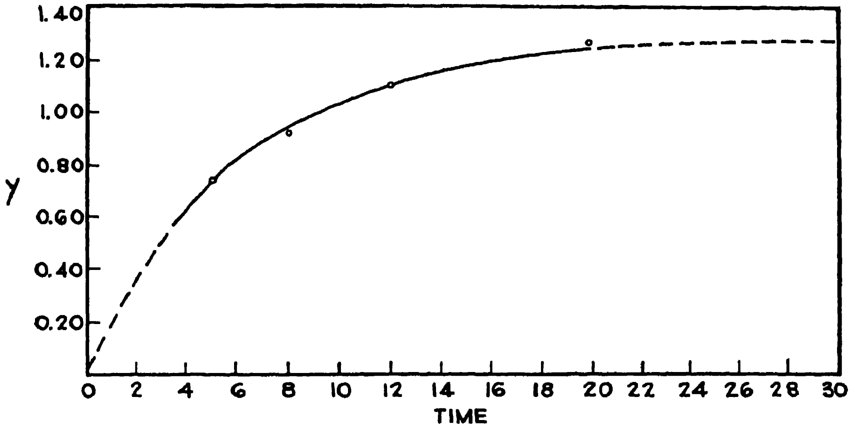


FIG. 107. γ, t curve.

If two sensitometric strips are developed, one for twice the time of the other, so that $t_2 = 2t_1$, simultaneous equations are obtained which on solution give $\frac{\gamma_2 - \gamma_1}{\gamma_1} = e^{-kt_1}$, and therefore $\frac{1}{t}\ln\frac{\gamma_1}{\gamma_2 - \gamma_1} = k$. The value of k thus found can be substituted in the general equation $\gamma = \gamma_\infty(1 - e^{-kt})$ and will give the value of γ_∞. This method of computation will be satisfactory only if the value of t is chosen correctly, so that $\frac{\gamma_2}{\gamma_1}$ is somewhat less than 0.8. If it is greater than this, the inaccuracy of determination increases very rapidly. (See also Ch. XIX, p. 731.)

When duplicates of the series of exposed strips used for Table XXVIII and Figure 106 were developed in a solution to which had been added 1.19 grams per liter of potassium bromide (*N*/100), the results are represented by the curves in Figure 108.

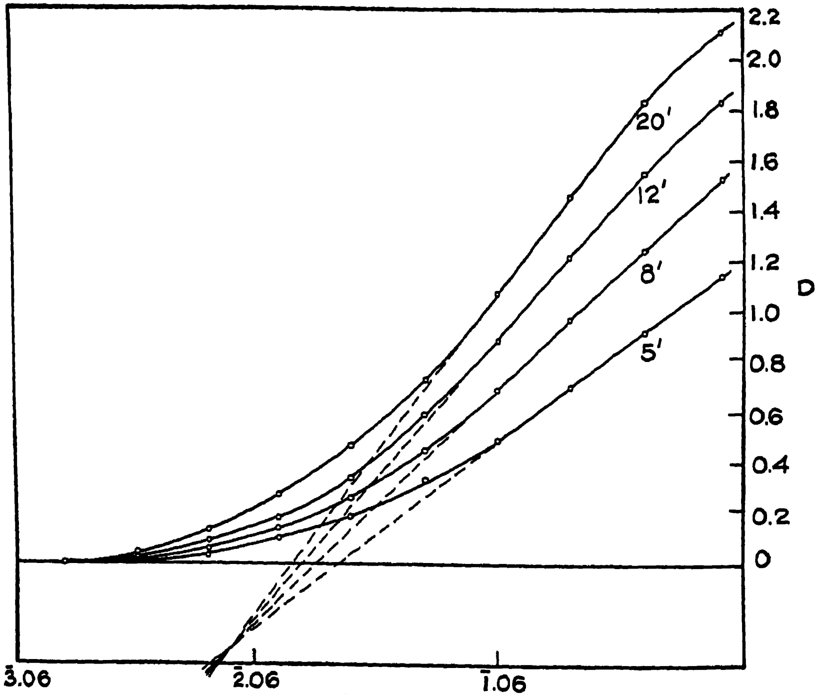


FIG. 108. Characteristic curves from strips developed in a bromided developer.

It is seen that the effect of bromide is to shift the straight lines parallel to their former position to cut the axis at points corresponding to greater exposures. Also, the straight-line portions of the curves still intersect at a point, but this point is below the regular log *E* axis. These effects of bromide in the developer were first pointed out by Hurter and Driffield [6] and were discussed in detail by Sheppard and Mees [2] and by Nietz.[4]

Sheppard and Mees studied the effect of bromide in ferro-oxalate developers. Their experiments showed that with developers containing up to N/50 bromide, the development factor, γ, is unaltered, but log i is raised; that is to say, the depression of the density, D, is constant over a certain range. Above N/50, the effect on $\log i$ is relatively less, while γ is now lowered so that there is no longer a period of constant depression. This and the consequent raising of $\log i$ become less as the time of development is increased, and on ultimate development disappear. In consequence, a definite *regression of the inertia* takes place. The shift $\Delta \log i$ from the data obtained appears to be directly proportional to the concentration of the bromide and inversely proportional to the time of development, as seen in Table XXIX.

TABLE XXIX (Sheppard and Mees)

	$P = \Delta \log i \times$ *time of development*		
Time, t	*P for N/200 K Br*	*P for N/100 K Br*	*P for N/50 K Br*
4.0 mins.	0.52	1.20	2.08
5.0 mins.	. .	1.00	2.16
6.0 mins.	0.54	1.35	1.72
8.0 mins.	0.53	. .	. .
12.0 mins.	0.50	1.08	1.50

It is possible from these data to give correction formulas for the effect of bromide on the exposure and development curves. For the exposure,

$$D = \gamma \log \frac{E}{i} - \frac{114N}{t},$$

where N is the normality of the bromide and t, the time of development. The effect on the development curve is similarly obtained. Without bromide, $D = D_\infty(1 - e^{-kt})$, and the addition of bromide results in the correction term, $\frac{k'\text{Br}}{t}$, so

$$D = D_\infty(1 - e^{-kt}) - \frac{k'\text{Br}}{t}.$$

Sheppard and Mees concluded that the nature of the retardation of the growth of density by bromide could be expressed as follows:

> "Whilst with no bromide every density grows proportionately from the start, bromide causes an initial induction- or retardation-period, the length of which depends both on the exposure and the bromide concentration."

Sheppard and Mees pointed out that development is essentially a reversible chemical reaction. This was demonstrated very definitely by them for the ferro-oxalate developer which they used. Other developers are not reversible in the same sense since, in most cases, the first oxidation products which could produce a reverse reaction are removed from the solution. Considering the reversibility of the ferro-oxalate developer, Sheppard and Mees wrote:

> "The course of chemical reactions in heterogeneous systems is likely to be very complicated, unless one of the processes is relatively far slower than the others. Nernst's theory[7] assumes that diffusion determines the velocity; but this is not always the case, and other conceptions are then necessary. A very comprehensive theory of reaction velocity in heterogeneous systems was advanced by Wilderman,[8] in which, however, diffusion is not considered. On the basis of this theory, it can be shown that, neglecting the 'invasion' of the developer, the course of the reaction is still represented by much the same function of the density of the image, while the existence of the reverse reaction can give rise to an induction period, which experiments demonstrate.[9] The process of development may be formulated as follows:

$$\begin{tikzcd}
\mathrm{Ag^+ + Br' + Fe(C_2O_4)_2''} \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, shift left] & \mathrm{Ag\ (in\ solution) + Br' + Fe(C_2O_4)_2'} \arrow[d, shift left] \\
\mathrm{AgBr\ (in\ solution)} \arrow[u, shift left] \arrow[d, shift left] & \mathrm{Ag\ (solid)} \arrow[u, shift left] \\
\mathrm{AgBr\ (solid)} \arrow[u, shift left] &
\end{tikzcd}$$

> "The various processes may be considered as follows. For the rate of solution of the silver bromide, we have

$$\mathrm{AgBr} \rightleftharpoons \mathrm{AgBr\ (in\ solution)}$$

$$\frac{dC}{dt} = K(C_0 - C)S^*$$

where C_0 = saturation or equilibrium concentration,
C = concentration at time t,
S = surface of silver bromide.

> "For AgBr in solution $\rightleftharpoons \mathrm{Ag^+ + Br'}$

$$\frac{d\,\mathrm{Ag}^+}{dt} = \frac{d\,\mathrm{Br}^-}{dt} = K'C - K''C_{\mathrm{Ag}^+}C_{\mathrm{Br}^-}$$

---

* The symbols in these equations have been changed to make them clearer.

"For the reduction,

$$\frac{d\,\text{Ag}}{dt} = K''[\text{Fe}''][\text{Ag}^+] - K'''[\text{Fe}'][\text{Ag}]$$

"And for the precipitation or solution of metallic silver

$$\frac{d\,\text{Ag}}{dt} = K^{\text{iv}}S'(C_0' - C'')$$

"Silver is precipitated or dissolved according as its concentration is above or below saturation. But if S', the surface, be nil, metallic silver will still be precipitated at a certain concentration, so that Wilderman introduces an 'instability constant,' say I, and we have

$$\frac{d\,\text{Ag}}{dt} = K^{\text{iv}}(S' + I)(C_0' - C'')$$

"Assuming a certain state of balance among these simultaneous reactions, a general equation may be obtained integrable under certain conditions. We have further to consider the supply of reducer by diffusion,

$$-\frac{d\,\text{Fe}''}{dt} = \frac{a\Delta}{\delta}(D_\infty - D)$$

"It is obvious that unless one action be entirely predominant by reason of its slowness, the velocity-curve will be complicated, as in graded homogeneous reactions."

An explanation of the way in which bromide produces a retardation at the initiation of development depends upon the theory which has been adopted regarding the initiation of development. If it is considered that the developer forms a saturated solution of metallic silver, the precipitation of which depends upon the presence of the latent image, then it is clear that the addition of bromide to the solution will lower the solubility of the silver halide and diminish the concentration of silver ions available for reduction. If, however, the developer actually attacks silver halide in the solid state, the effect of bromide will depend upon its influence upon this reaction between the two phases the reducing developer in solution and the solid silver bromide. (For the mechanism of such reactions, see Chapter VIII.)

Nietz studied at length the depression of density as a result of the presence of bromide in the developer. As has already been pointed out, the effect of bromide is to depress the intersection point of the straight-line portions of the curves below the log E axis. Nietz adopted as the best criterion for the exist ence of a common intersection point the relation between the density and γ. If this curve is a straight line, the straight-line portions of the characteristic curves intersect at a point, and if the line passes through the origin, this point is on the log E axis. If, further, the D, γ curve is a straight line but does not pass through the origin, then the straight-line portions of the characteristic curves meet at a point which is not on the log E axis. The abscissa co-ordinate of this point may be termed a, and the ordinate, b. An experiment of Nietz' is shown in Figure 109,

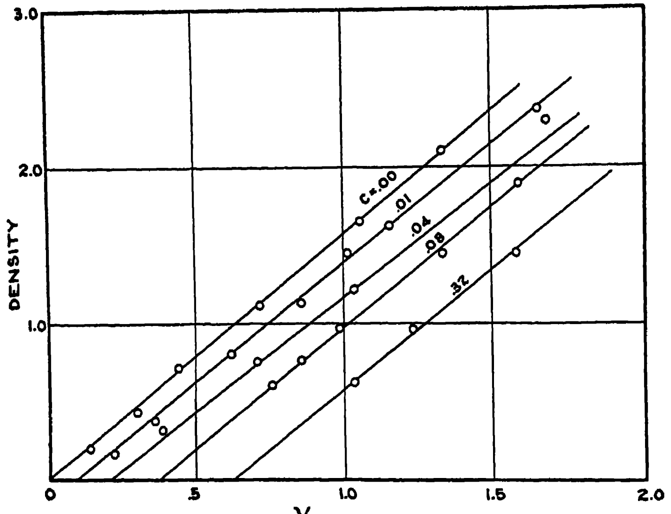


FIG. 109. D, γ curves for paraminophenol developer with varying concentration of bromide.

the developer being M/20 p-aminophenol using various concentrations of bromide. It is seen that all the D, γ curves are straight lines and that, as the bromide concentration increases, the lines recede from the origin, corresponding to the depression of density for the same γ and indicating that the intercept of the straight-line portions of the curves is depressed below the log E axis. In Figure 110 is given a general case showing the depression of the point of intersection. From this,

$$d = WN = WT + TN;$$

$$\frac{WT}{TM} = \gamma; \quad WT = (TM)\gamma = (a_2 - a_1)\gamma;$$

$$TN = -b_2 + b_1.$$

Therefore,

$$d = -b_2 + b_1 + (a_2 - a_1)\gamma.$$

If the a and b values for zero concentration of potassium bromide are called a_0 and b_0, the density depression, d, is given by

$$d = -b + b_0 + (a - a_0).$$

But, for the normal case, $b_0 = 0$ and $a = a_0$. Therefore, the depression caused by the concentration of potassium bromide, C, is

$$d = -b,$$

and this is independent of γ. If, now, the density depression, d, as measured in this manner is plotted against the logarithm of the corresponding bromide concentration, a straight line is obtained whose equation may be written

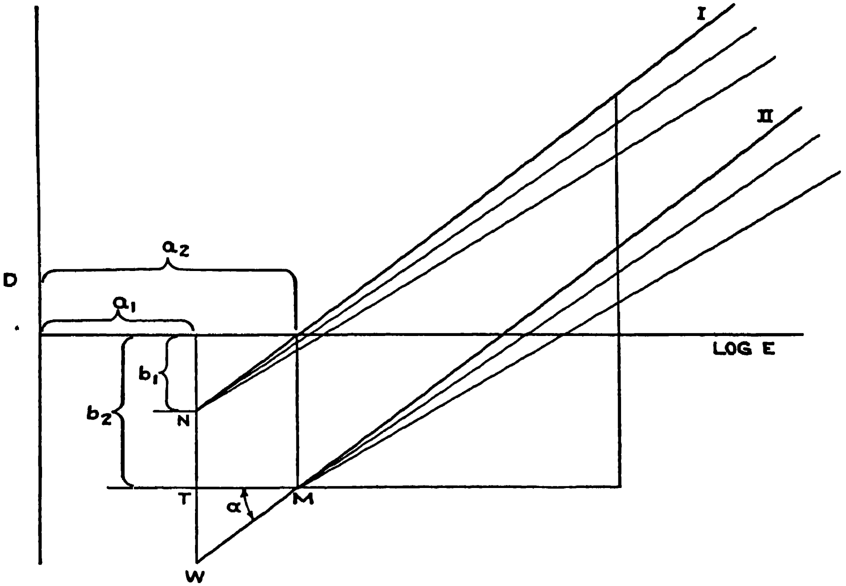


FIG. 110. Generalized characteristic curves showing the depression of the inertia point due to bromide.

$$d = m(\log C - \log C_0),$$

m being the slope and $\log C_0$ the intercept on the $\log C$ axis. Nietz found that all these d, $\log C$ curves, in which the depression of the intersection point is plotted against the logarithm of the concentration of bromide, show the same slope, the slope m being 0.43. The evidence which Nietz presents for this seems to be somewhat doubtful, and there is, at any rate, some considerable evidence that hydroquinone persistently shows a higher slope for the d, log C curves than the other developers; but Nietz considered that he was justified in assuming that the slope m is independent of the emulsion and of the developer used, that is, that the rate of change of depression with the bromide concentration is independent of the emulsion, the developer, and the bromide concentration itself. If this is so, then, for any two developers, a comparison of the C_0 values at which the same depression is produced can be used to show the resistance of the developers to the effect of bromide.

Sheppard[2] first suggested that if the depression in density produced by bromide is a measure of the activity of the developer, the depression could be used to give a dynamic method of measuring the energy of a developing agent, since its effect should be a function of the natural potential of a developer in relation to its oxidation product. Thus, it was found that the concentration of bromide required to produce the same depression as N/100 potassium bromide in the ferro-oxalate developer was 0.0113 for hydroxylamine; 0.0052 N for hydroquinone at 34 per cent development and 0.0070 N at 40 per cent development; and 0.034 N for p-aminophenol. These values were taken as expressing the relative reducing energies of the developers compared with ferro-oxalate. It is seen that p-aminophenol is much the most energetic of those tried; next comes hydroxylamine; while hydroquinone has only from one-half to two-thirds the energy of ferrous oxalate.

The results for alkaline development obtained by Sheppard are numerically tabulated under the following terminology:

k = velocity of development per gram molecule at 20° C.

$$= \frac{1}{t} \log_{10} \frac{\gamma^{\infty}}{\gamma^{\infty} - \gamma}.$$

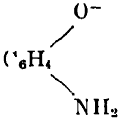
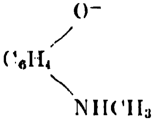
E = efficiency, *i.e.*, velocity of development compared with ferrous oxalate at 20° C., divided by R.

R = reducing power, *i.e.*, gram molecules of silver bromide reduced by one gram molecule of reducer.

T.C. = temperature coefficient $= \dfrac{k_T + 10^\circ}{k_T}$.

F = energy = concentration of bromide producing the same retardation as is given by 0.01 N potassium bromide with ferro-oxalate.

Summary of Various Factors Relating to the Properties of Developers (Sheppard)

Developer	*R*	*k*	*E*	*T.C.*	*F*
Ferro-oxalate $Fe(C_2O_4)_2^{=}$	1	0.061	1.00	1.70	$0.01\ N = 1.00$
Hydroxylamine NH_2O^-	1	0.305	5.0	2.10	$0.0113\ N = 1.13$
Hydroquinone $C_6H_4O_2^{=}$	2	0.146	1.20	2.80	$0.0052\ N = 0.52$ $0.0070\ N = 0.70$
p-Aminophenol  $C_6H_4(O^-)(NH_2)$	(2)	0.550	4.5	1.50	$0.034\ N = 3.4$
Metol  $C_6H_4(O^-)(NHCH_3)$	(2)	0.500	4.4	1.25	..

Extending this work, Nietz calculated from his values for C_0 the relative bromide potential, π_{Br}, as follows:

> "The greater the value of C_0, the lower the bromide sensitivity of the developer. Hence,
>
> $$\text{bromide sensitivity} \propto \frac{1}{C_0}.$$
>
> But the greater the value of C_0, the greater the bromide potential. Therefore,
>
> $$\pi_{Br} = f(C_0), \text{ which is possibly } \pi_{Br} = K \log C_0.$$
>
> But for the time being this is arbitrarily defined as
>
> $$\pi_{Br} = KC_0.$$

"At present there is no means for determining this constant K. The bromide potential of a developer X will be $(\pi_{\text{Br}})_x = K(C_o)_x$; that for a given standard developer will be $(\pi_{\text{Br}})_{\text{Std.}} = K(C_o)_{\text{Std.}}$ Consequently the relative bromide potential, π_{Br}, for any developer X referred to a given standard is

$$\pi_{\text{Br}} = \frac{(\pi_{\text{Br}})_x}{(\pi_{\text{Br}})_{\text{Std.}}} = \frac{K(C_o)_x}{K(C_o)_{\text{Std.}}} = \frac{(C_o)_x}{(C_o)_{\text{Std.}}}."$$

This relation was used by Nietz for obtaining the values of π_{Br} for a large number of developing agents (Chapter IX, p. 352).

There is little doubt that the amount of depression in the developed density produced by the addition of bromide to a developer is of significance as a measure of some expression of the activity of the developer. At the same time, the numerical results obtained in a limited study of the subject are of somewhat doubtful validity, and much further work is required to obtain results having definite value, especially in relation to the chemical structure of the developing agents.

Nietz found that the velocity ratios of developers are approximately proportional to their bromide potentials, as shown in Table XXX.

TABLE XXX

RELATIVE POTENTIALS (Nietz)

	From velocity ratios	π_{Br}
Pyrogallol	13	16
Dichlorhydroquinone	11	. .
Dimethyl-*p*-aminophenol	10	10
p-Amino-metacresol	9.5	. .
Bromhydroquinone	8.4	21
Dibromhydroquinone	8	. .
p-Amino-orthocresol	7	7
Chlorhydroquinone	7	7
Toluhydroquinone	7	2.2
p-Aminophenol	6	6
Ferro-oxalate	5.7	0.3

In the study of the chemistry of development, it is of great importance to determine D_∞ with as much precision as possible, but from the photographic point of view, the determination of γ_∞ is most important since this is a property of the photographic material itself. While it is dependent to some extent upon the development, the variation in the value of γ_∞ among photographic materials is of extreme importance as conditioning the properties and uses of these materials. As has been pointed out already, γ_∞ can be determined experimentally with bromided developers, and it may be computed also with considerable accuracy if D_∞ is known and the co-ordinates of the intersection point of the straight-line portion of the characteristic curves for different times of development are also known. The relation between density and γ is expressed as

$$D = \gamma(\log E - a) + b.$$

From data on the D, γ relation, especially with bromide, where upon prolonged development γ_∞ is closely approached, there is every reason to believe that this relation holds at the limit; that is,

$$D_\infty = \gamma_\infty(\log E - a) + b;$$

from which

$$\gamma_\infty = \frac{D_\infty - b}{\log E - a}.$$

Consequently, γ_∞ may be calculated if D_∞ is known (from a velocity curve at some particular value of $\log E$) and the values of a and b are also known. In the complete study of an ordinary developer, all these can be determined with a fair degree of accuracy.

There is no doubt that some developers can reduce more silver for the same exposure than others and that the value of D_∞ and, consequently, of γ_∞ will depend upon the developer used.

Nietz determined the values of γ_∞ for several developers, of which he had also determined the relative bromide potential, π_{Br}, from the concentration of bromide required to give the standard depression of density. In his results, D_∞ and k were found by means of the equation $D = D_\infty(1 - e^{-k \log t/t_0})$ applied to the D, t curve for a fixed exposure, since he found this equation to hold much better than the equation $D = D_\infty(1 - e^{kt})$ (p. 428). a and b were found from D, γ curves for the same exposure, and γ_∞ was then computed from the equation above. In these first results Nietz found that D_∞ and γ_∞ increase with increasing π_{Br} (Table XXXI). Further work, however, showed

TABLE XXXI

BROMIDE POTENTIAL AND D_∞ FOR VARIOUS DEVELOPING AGENTS (Nietz)

Developer	π_{Br}	D_∞	γ_∞
M/25 Bromhydroquinone	21	3.7	2.29
M/20 Monomethyl-*p*-aminophenol sulfate	20	3.9	2.33
M/20 Chlorhydroquinone	7	2.7	1.62
M/20 *p*-Aminophenol hydrochloride	6	3.2	1.99
M/20 Toluhydroquinone	2.2	3.3	1.75
M/20 *p*-Phenylglycine	1.6	2.8	1.55

that D_∞ and γ_∞ do not always increase with π_{Br}. Thus hydroquinone, though a developer of high bromide sensitivity (low π_{Br}), can produce high maximum density and contrast. Nietz extended this work to a great range of developers, with which he developed exposed strips of the same material, and since his results, and especially the values of D_∞ which he obtained, are of interest, they are given in Table XXXII (p. 423).

This table does not by any means show that D_∞ always varies with the values of π_{Br} obtained by the method adopted. But, by this method, developers may be compared on a basis which is more or less independent of the observer, the degree of development, and numbers of special factors; and it is quite certain that several definite tendencies are indicated. These may be summarized as follows:

D_∞ and γ_∞ for a single emulsion may vary greatly with different reducing agents.

The value of the maximum density, D_∞, tends to be greater the higher the bromide potential of the developer. Exceptions to this rule may be accounted for in a number of ways, on none of which is there definite information.

γ_∞ shows an unordered variation with any of the properties of the reducing agents. The lowest values are obtained for developers of the lowest bromide potential, but this relation does not hold with higher values. The intersection points of the characteristic curves show similar unsystematic shifting. Because the inertia value is a function of some other property than the bromide potential of the reducing agent, γ_∞ is also. For developers giving about the same inertia value, γ_∞ tends to be higher with increasing potential.

TABLE XXXII

Bromide Potential and Other Factors for Various Developing Agents (Nietz)

Developer	D_∞	π_{Br}	γ_∞	k	t_0
M/20 Toluhydroquinone	4.40	2.2	1.67	.63	1.35
Diaminophenol plus alkali	4.2	40.0	1.40	.60	0.6
p-Aminophenol	4.2	6.0	1.84	.44	1.0
p-Amino-metacresol	4.0	9.0	1.33	.72	1.24
Methyl-*p*-amino-orthocresol	4.0	23.0	1.26	.60	.33
Pyrogallol	4.0	16.0	1.22	.57	0.78
Chlorhydroquinone	4.0	7.0	1.82	.52	1.3
Hydroquinone	3.8	1.0	1.26	.95	1.80
Dibromhydroquinone	3.8	8.0	1.27	.80	0.80
p-Amino-orthocresol	3.8	7.0	1.27	.70	0.87
Bromhydroquinone	3.8	21.0	1.73	.66	1.27
Eikonogen	3.8	..	1.43	.47	1.7
Monomethyl-*p*-aminophenol	3.6	20.0	1.50	.58	.70
Diaminophenol, no alkali	3.6	..	1.63	.55	.36
Catechol	3.6	..	1.68	.52	.60
Dichlorhydroquinone	3.6	11.0	1.29	.53	.80
Edinol	3.6	..	1.22	.46	1.9
Phenylhydrazine, no alkali	3.5	1.0	..	.03	8.5
Dimethyl-*p*-aminophenol	3.2	10.0	1.18	.61	0.75
Ferro-oxalate	3.1	0.3	1.29	.55	0.97
Benzyl *p*-aminophenol (Duratol)	2.4	less than 5	0.98	.34	2.27
p-Phenylenediamine	1.7	0.4	0.58	.34	2.10

The unsubstituted aminophenols stand at the head of the list in Table XXXII; next, the hydroxybenzenes and their halogen substitution products; and the amines are at the bottom.

Hydroquinone and its mono- and di-chlor- and brom-derivatives seem to be nearly identical in this classification, though their bromide potentials vary greatly. This may be because the mechanism of their oxidation is the same, while other conditions also are similar and mask any effect of potential.

Most cases which show a systematic variation of D_∞ with bromide potential also show systematic variation in what is erroneously termed the "rapidity"; that is, the time required to develop a definite intermediate density. The densities developed in, say, two minutes for each case tend to be in the same order as the values of D_∞. This is evident from the character of the equation $D = D_\infty(1 - e^{-k \ln t/t_0})$, since if k and t_0 are nearly constant, the density for a fixed time will vary with D_∞. From the data given, it is seen that the variation in k is not great and that for many compounds t_0 also does not vary widely.

A close relation between the rate of development and the final density is to be expected, since the final density, D_∞, is a function of this rate. It must be remembered (Chapter IV, p. 138) that each grain in which development is started is developed out to complete development with most developers. The final density, D_∞, is that of the completely developed grains for which the developer could start development. Where the same mechanism of development prevails, the number of these grains varies with the activity of the developer: the more active developers attack even slightly exposed grains, which stay undeveloped in weaker developers. One of the main criteria for a good developer is a sharp difference in reaction rate for the developable and the undevelopable grains at whatever size of the latent image this limit exists. This selectivity, which is discussed on p. 455, was chosen by Shiberstoff [10] as one of the various properties of practical importance, by which developers could be classified quantitatively. It is designated by him as U and is intended to define the relation of the rate of development of the image to the rate of development of fog.

Shiberstoff studied the measured sensitivity of an emulsion in relation to the developer used. Nietz [4] found a very wide range in the effective sensitivity of a material according to the developer used but considered that the variation of the emulsion speed, as it was determined by his sensitometric procedure with different developing agents, was far from orderly; he concluded that, on the whole, the effective speed increases somewhat with the increasing reduction potential.

Cheltzoff and Krashenimikova [11] also measured the variation caused by the developer in the values obtained for sensitivity and found a maximum variation of about three to one. Shiberstoff found that for the range of developers which he used, there is a variation of only about one to one and one-half. He gives the following table for results found by the three workers:

TABLE XXXIII

EFFECT OF THE DEVELOPING AGENT ON SENSITIVITY

Nietz		*Cheltzoff and Krashenimikova*		*Shiberstoff and Bukin*	
p-Aminomethylcresol	100	Adurol	79	Eikonogen	31.5
Pyrogallol	76	Metol	60	Pyrogallol	30.1
Hydroquinone	46	Hydroquinone	54	Adurol	29.4
Eikonogen	18	*p*-Aminophenol	50	Catechol	26.8
Metol	10	Pyrogallol	47	Hydroquinone	25.1
p-Aminophenol	7.6	Amidol	35	Glycin	25.1
Adurol	6.3	Catechol	29	Metoquinone	24.4
Amidol	6.3			Metol	22.7
Catechol	5.5			*p*-Aminophenol	17.6

In this table the figures are supposed to represent determinations, using different developing agents, of the "sensitivity" of a selected material. The three sets of determinations, however, are not comparable, and the use of different materials would give very different results. Nietz expresses his disbelief in the general validity of his results.

From the sensitivity and maximum γ, which vary somewhat with the developing agent, Shiberstoff computed a coefficient for the effectiveness of a developer which he calls the degree of "perfection,"

$$W = K \cdot S_{\gamma_\infty} \cdot \gamma_\infty.$$

He concludes that *p*-aminophenol, glycin, and catechol are of the highest degree of "perfection," and hydroquinone is the least perfect of developers, while the commonly used metol hydroquinone, metol, and pyrogallol developers are intermediate. He points out, however, that in practical work, a most important factor is the velocity of development, so that a developer of moderate "perfection," having greater velocity, is to be preferred. He introduces a new concept, the degree of "practicability" (P), where $P = \frac{W}{t_{\gamma_\infty}}$. Developers arranged in order of descending P are given in Table XXXIV from Shiberstoff's paper.

It should be pointed out that the determination of coefficients such as W and P for general application would require an enormous amount of work, since it would be necessary to establish them not only for developing solutions of a wide range of composition but also for a great number of different emulsions. It is very doubtful indeed whether any generalization could be drawn, though it is possible that the measurement of these coefficients for a given emulsion and a given series of developers of similar composition would have some value.

TABLE XXXIV

THE "PRACTICABILITY" OF DEVELOPERS (Shiberstoff)

	P (15° C.)
Metoquinone and metol hydroquinone	69.1
Metol	58.6
Pyrogallol	55.0
p-Aminophenol	52.1
Bromhydroquinone	35.3
Catechol	33.6
Eikonogen	30.8
Chlorhydroquinone	28.0
Glycin	27.6
Hydroquinone	14.7

THE EQUATIONS EXPRESSING THE VELOCITY OF DEVELOPMENT

As is shown on page 406, the equation which expresses the course of development of a density for the simplest case was found by Hurter and Driffield and Sheppard and Mees to be:

$$kt = \ln \frac{D_\infty}{D_\infty - D} \quad \text{or} \quad D = D_\infty(1 - e^{-kt}). \tag{1}$$

It is hardly to be expected that the course of so complicated a process as photographic development in the presence of alkali could be described by so simple a law, since changes at various stages are known to exist. Even if equation (1) held approximately over a considerable range, there would be possibilities of several complications which might increase in importance as time went on or would be of more importance in the early stages of the process. For example, it is unlikely that diffusion of the developer into the gelatin emulsion and of the reaction products out of it is the simple process assumed. Through adsorption and various other physical phenomena, relatively large local changes may occur in the concentration of the developer. In such a case, development might approximate a second-order reaction, the velocity being proportional both to the mass of latent image remaining to be reduced and to the concentration of the developer; that is, the quasi-bimolecular form,

$$\frac{dD}{dt} = k(D_\infty - D)(A - B), \tag{2}$$

may be a more nearly correct expression. A is the concentration of the developer at the beginning, and B equivalents were used at the time t. The integrated form is

$$k = \frac{1}{t} \ln \frac{D_\infty(A - B)}{(D_\infty - D)A}. \tag{3}$$

If, over a range of times, B is small compared with A (and this is often the case since a very small amount of silver is formed compared with the amount of developing agent present), $\frac{A - B}{A}$ will be nearly equal to unity, and the last equation becomes practically the first-order form. But, if, by tanning of the gelatin or other mechanical means, inclusion of the developer occurs, so that its local concentration changes as time goes on, then a gradual departure from the first-order law takes place. Something like this does occur, but the phenomena are undoubtedly more complex than the above explanation suggests.

It is not impossible that two successive reactions of the first order take place and give rise to disturbing influences at the beginning. As Mellor points out, if k_1 and k_2 for two such reactions are widely different, the general trend of the reaction is a close approximation to a single first-order reaction after initial disturbances, and the sooner they take place, the greater the ratio k_1/k_2. The simple equation (1) fits the data only for those cases where the time of appearance of the image (p. 433) is short, and then only for the early stages; that is, the development reaction follows the first-order law for a time, but this law does not completely describe the process. In case the time of appearance is long and there is a considerable induction period, the velocity equation can be corrected to some extent by allowing for the initial period of inactivity, as was suggested by

Sheppard. This can be done by introducing into the equation the time of induction t_0. Thus, the velocity equation becomes

$$k(t - t_0) = \ln \frac{D_\infty}{D_\infty - D}$$

or, in exponential form, $D = D_\infty(1 - e^{-k(t-t_0)})$. The differential form of these equations is, of course, unchanged:

$$\frac{dD}{dt} = k(D_\infty - D).$$

Nietz showed that while this equation with its correction for the induction time fitted the observed increase of density with time in the earlier stages of development, it failed to represent the later course of the reaction, so that the simple velocity equation in which the induction period is taken into account is still not entirely satisfactory as representing the reaction. Nietz pointed out that in the great majority of cases, the function $\ln \frac{D_\infty}{D_\infty - D}$ would give a straight-line relation over a considerable range when plotted against the logarithm of the time instead of the time itself. He proposed that this relation should be used both as giving an improved equation for the representation of the velocity of development and as a method of determining the effective value of D_∞.

When $\log \frac{D_\infty}{D_\infty - D}$ is plotted against $\log t$,* as just described, the equation for the straight line is

$$k(\log t - \log t_0) = \log \frac{D_\infty}{D_\infty - D},$$

the slope being k, as before, and the intercept on the $\log t$ axis, $\log t_0$. In the exponential form, this is

$$D = D_\infty(1 - e^{-k \log t/t_0}),$$

which, differentiated, becomes

$$\frac{dD}{dt} = \frac{k}{t}(D_\infty - D).$$

---

* In practical sensitometry, the value of k is adjusted for the use of common logarithms, and the transition from natural logarithms is made here to correspond with the values given by Nietz.

This last equation shows that the velocity is inversely proportional to the time, a fact for which there is no satisfactory explanation. It is possible that this change of the velocity as the development proceeds may be due to the accumulation of oxida-

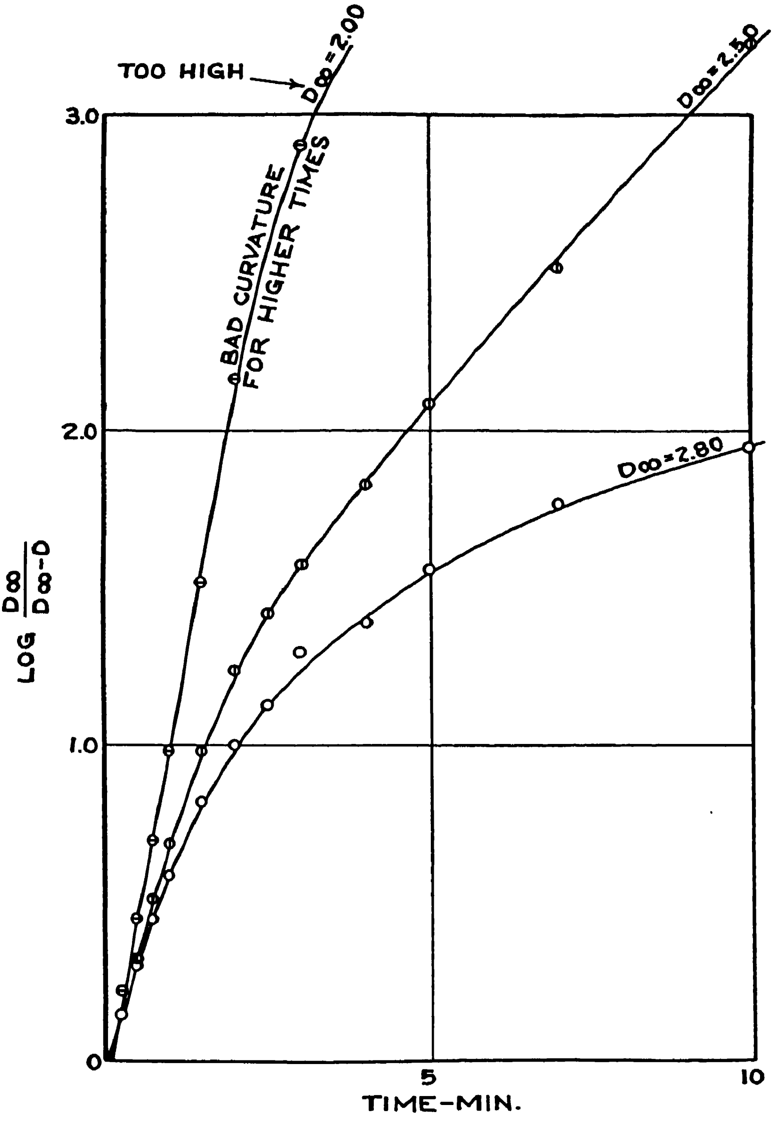


FIG. 111. Plot of log $\frac{D_\infty}{D_\infty - D}$ against time of development.

tion products and of bromide ions. *k* no longer has the same meaning as in the simple velocity equation for development. Nietz gives an example of the method in which a group of data

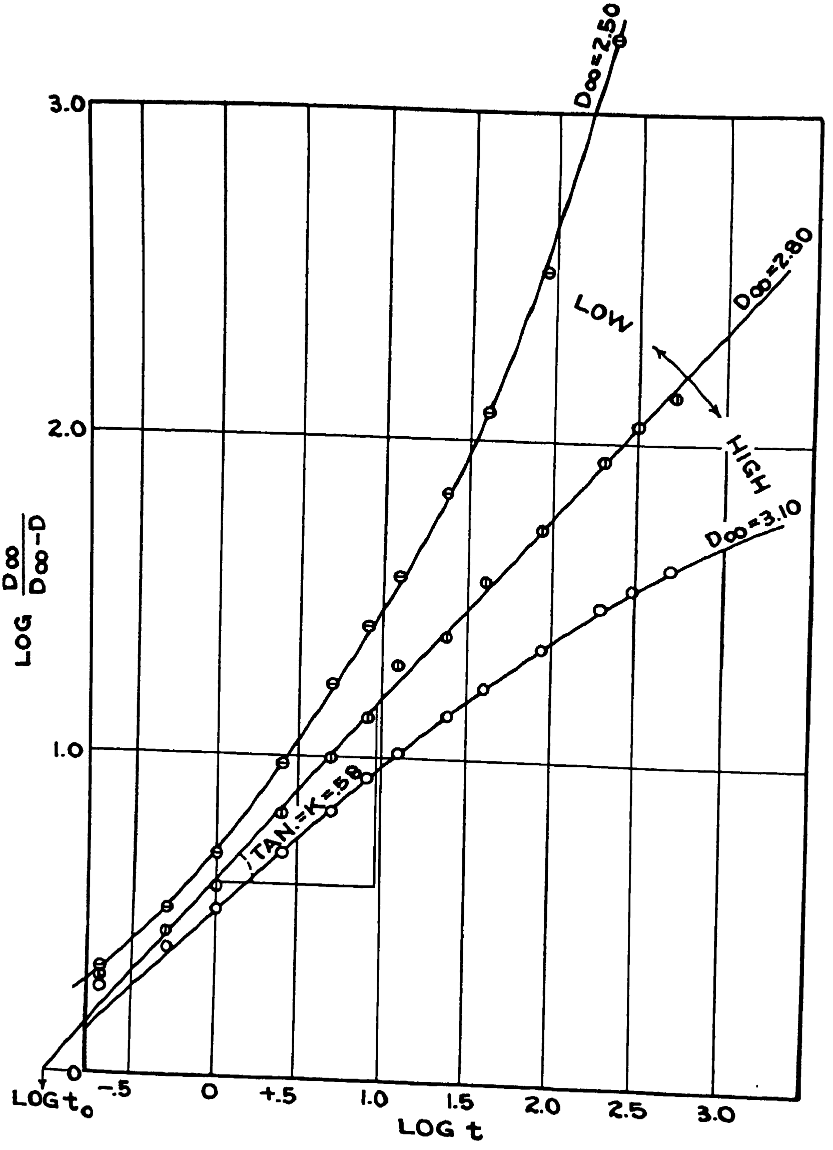


FIG. 112. Plot of log $\frac{D_\infty}{D_\infty - D}$ against log *t*.

could be fitted with an equation of this form. This, of course, involves the choice of a suitable value for D_∞.

The experimental material was derived from a series of developments carried out with monomethyl *p*-aminophenol sulfate, a developer which Nietz found to show wide departure from the first-order equation

$$\frac{dD}{dt} = k(D_\infty - D).$$

The observed densities are plotted against the time of development, and a smooth curve is drawn. Then, using the data from the smooth curve, several estimates were made of D_∞, and the values of $\log \frac{D_\infty}{D_\infty - D}$ were computed and are plotted against the time of development in Figure 111. The value of D_∞ used for each curve is shown in the figure. It is evident that even the value 2.00 is too high to produce a straight line over any range, and yet this value was reached experimentally after about three minutes' development.

In Figure 112, the values of $\log \frac{D_\infty}{D_\infty - D}$ are plotted against $\log t$ instead of against t, and it is seen that a value for D_∞ of 2.80, which is a reasonable value from the data, gives a straight line over the entire range observed. For the value $D_\infty = 2.80$, therefore,

$$k(\log t - \log t_0) = \log \frac{D_\infty}{D_\infty - D},$$

in which the constants are as follows:

$$\begin{aligned} k &= 0.58; \\ D_\infty &= 2.80; \\ \log t_0 &= -1.05; \\ t_0 &= 0.11. \end{aligned}$$

Putting the equation above in the exponential form,

$$D = D_\infty(1 - e^{-k \log t/t_0});$$

and computing densities by means of it, with the constants indicated, they agree very well with the experimental results obtained. Obviously, it is unnecessary to go to the additional labor of computing densities, since the curve of $\log \frac{D_\infty}{D_\infty - D}$ plotted against $\log t$ indicates the nature of the agreement.

R. B. Wilsey suggested the following modification of the Nietz formula:

$$D = D_\infty(1 - e^{-k(t-t_0)^b}).$$

This naturally describes the development process more clearly from beginning to end, since it is more complex and contains an additional constant b. In most cases, the equation yields practically the same value for D_∞ as Nietz' equation.

The four forms of the velocity equation which have generally been applied may be summarized in the table shown below. In addition to this, a number of more complex forms have been suggested in order to represent the extremely complicated course of development as closely as possible.

TABLE XXXV

FORMS OF VELOCITY EQUATION USED

	Log Form	*Exponential Form*	*First Derivative = Velocity*	*Author*
I	$kt = \log \frac{D_\infty}{D_\infty - D}$	$D = D_\infty(1 - e^{-kt})$	$\frac{dD}{dt} = k(D_\infty - D)$	Applied to photographic material by Sheppard and Mees
II	$k(t - t_0) = \log \frac{D_\infty}{D_\infty - D}$	$D = D_\infty(1 - e^{-k(t-t_0)})$	$\frac{dD}{dt} = k(D_\infty - D)$	Correction applied to I by Sheppard
III	$k(\log t - \log t_0)$ $= \log \frac{D_\infty}{D_\infty - D}$	$D = D_\infty(1 - e^{-k \log t/t_0})$	$\frac{dD}{dt} = \frac{k}{t}(D_\infty - D)$ $= kt^{-1}(D_\infty - D)$	Nietz
IV	$\log k + b \log(t - t_0)$ $= \log \log \frac{D_\infty}{D_\infty - D}$	$D = D_\infty(1 - e^{-k(t-t_0)^b})$	$\frac{dD}{dt} = kbt^{b-1}(D_\infty - D)$	Wilsey

THE EFFECT OF THE COMPOSITION OF THE DEVELOPER UPON THE VELOCITY OF DEVELOPMENT

The velocity of development depends, of course, upon the composition of the developing solution. The effects of the total concentration of the solution, of the concentration of the developing agent, the sulfite, the alkali, and the bromide, have been investigated for a number of developers. Hurter and Driffield[6] studied the effect upon the progress of development of the composition of the ferro-oxalate developer and of pyrogallol developers, using ammonia and soda as the alkalis. Sheppard and Mees studied ferro-oxalate, hydroxylamine, *p*-aminophenol, and hydroquinone, while Nietz studied the hydroquinone and methyl *p*-aminophenol developers.

A simple method of great value in the study of the effect of components and concentration of the developer upon the velocity of development is the determination of the time of appearance of the image. Watkins[12] showed that for any given reducer, the time of appearance of the image is proportional to the time required to obtain a given degree of development; any variation in concentration, temperature, and so forth affecting the time necessary to reach a given density or development factor affects the time of appearance in the same proportion. Thus,

$$t_D = W \times t_a,$$

where

t_D = the time to obtain the density, D,

t_a = the time of appearance,

and

W = a constant known as the *Watkins Factor.*

When photographic materials were not sensitive to red light and the time of appearance could, therefore, be watched by means of the darkroom lamp, this rule formed a valuable guide to the time of development because, to a considerable extent, the time of appearance does vary in proportion to the total time of development for differences in temperature and in the photographic materials used. The statement is not true in general, however, and if conditions are changed with complex developing solutions, it cannot be considered valid.

Sheppard and Mees[13] give the following explanation of the Watkins' rule and of the limitations to its validity:

> "The density, θ, first visible, is a small but constant fraction of the total density, being a psychological constant—a threshold value of perception. For the same exposure, θ measures an equal fraction of the total change; for the same developer, with different exposures, it is the same fraction of the oxidation of the developer. Now, if two analogous reactions proceed to equal fractions of the total change, the correlated times are inversely as the velocity

> factors. Hence, if D_1 and D_2 are two final densities, and λ a fixed density less than these, while δ_1 and δ_2 are the times of appearance, t_1 and t_2 the respective times to reach the density λ, then $t_1/\delta_1 = t_2/\delta_2 = t_n/\delta_n =$ constant W, whose numerical measure is proportional to the Watkins multiple, and depends only on the velocity function. The general theorem is only true for simple reactions, and does not hold for 'graded,' 'catalysed,' and so forth. *The same limitations hold for development*, and the coupling of simultaneous reactions, or initial disturbances, varying with different reducers, are sufficient to account for the wide variation of the Watkins multiple, as well as its occasional inconstancy with the same developer. Deviations may occur for such a small fraction of the total change and yet the development function remain much the same."

For accuracy, it is necessary that time of appearance should be neither too short nor very long. In experimental work, a considerable amount of light may be used; since the later production of fog is usually not of importance, the timing may be carried out with a stop watch or, more conveniently, with a simple type of chronograph, using a key to mark the time of appearance. While the Watkins' factor is little affected by the concentration or temperature of the developer, it varies greatly with the bromide concentration.

For ferro-oxalate, Sheppard and Mees showed that the velocity constant, k, of the development equation is proportional to the total concentration of the developer. Provided that the concentration multiplied by the time is a constant, therefore, either may be varied independently and the same γ will be obtained. An experimental result obtained by Sheppard and Mees is given in the following table:

TABLE XXXVI

EFFECT OF THE CONCENTRATION OF A FERRO-OXALATE DEVELOPER ON DENSITY
(Sheppard and Mees)

	Density				
Log E	*Conc.* *N/5* *t* (*min.*) *1.5*	*N/10* *3.0*	*N/20* *6.0*	*N/40* *12.0*	*Mean*
2.48	..	1.358	1.440	1.446	1.414
2.19	1.302	1.248	1.278	1.270	1.274
1.89	1.094	1.114	1.104	1.120	1.108
1.61	0.892	0.892	0.902	0.850	0.884
1.26	0.604	0.688	0.676	0.708	0.644
1.05	0.442	0.436	0.428	0.358	0.414
0.83	..	0.244	..	..	0.244

Alkaline developers behave in approximately the same manner but, owing to the greater complexity of developing solutions containing organic developers, the time of development is not so strictly proportional to the concentration. In the case of alkaline development, there are three possible methods by which the effective concentration of the developer may be varied:

1. Change in the total concentration with the proportion of the different components of the solution remaining unchanged;
2. Change in the concentration of alkali;
3. Change in the concentration of the organic reducer.

Sheppard and Mees found that with developers such as hydroxylamine, hydroquinone, *p*-aminophenol, and methyl *p*-aminophenol, a change in the concentration of the solution could not be compensated by a proportional change in the time. Thus, with hydroxylamine, using N/20 solution and N/10 alkali, if the concentration was halved, the time of development for the same γ was $2\frac{1}{2}$ times as much. With *p*-aminophenol, the velocity was approximately proportional to the alkaline concentration with a constant excess of solution and nearly the inverse of the reducer when the alkali and the reducer were present in quarter-molecular proportions. Thus, measuring the time of appearance with quarter-molecular quantities for *p*-aminophenol hydrochloride, and sodium hydroxide in different volumes of water, they found the times of appearance given in the following table:

TABLE XXXVII

TIME OF APPEARANCE AND CONCENTRATION (Sheppard and Mees)

t_a *in Seconds*	*Volume V*	t_a/V	*Concentration*
5.0	1.0	5.00	*M*/20
10.3	2.0	5.15	*M*/40
21.0	4.0	5.25	*M*/80
39.6	8.0	4.90	*M*/160
81.0	16.0	5.06	*M*/320
247.4	32.0	7.73	*M*/640

It is seen that the initial velocity is proportional to the concentration until the concentration falls to about *M*/320, after which the velocity falls off more rapidly owing to either increased hydrolysis or a diminished potential.

A similar study of the effect of concentration of developing solutions on the rate of development was carried out by Nietz and Whitaker.[14] The developer used had the following composition:

Developing agents	*M*/20
Anhydrous Sodium Sulfite	50 grams
Anhydrous Sodium Carbonate	50 grams
Water to make	1 liter

Their results for three developing agents are shown in Figure 113. Curve *A* corresponds to methyl *p*-aminophenol; *B*, to pyrogallol; and *C*, to glycin. It is seen that the optical density obtained at first increases with dilution, then passes through a maximum, and decreases again if the product of concentration and time is held constant.

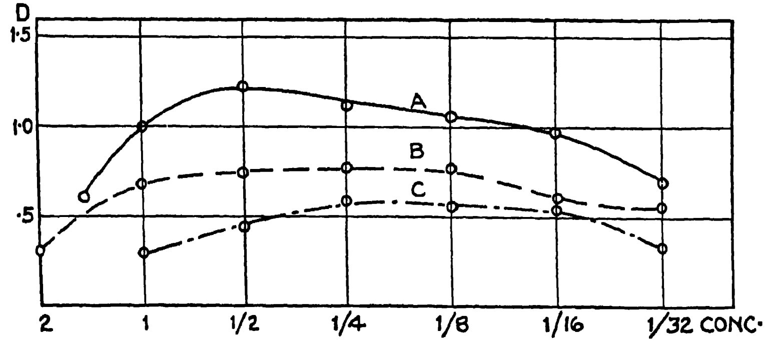


FIG. 113. Effect of the concentration of the developer on the rate of development.

The effect of the concentration of developer upon development was studied also by Chibisoff.[15] Using a methyl *p*-aminophenol developer, he found that the inertia is not affected by the concentration and only to a very small extent by the temperature of the developer, and that if a change in the concentration is compensated for by a change in time, the variation of γ with the changing concentration is small. This work was extended by Chibisoff and his collaborators to cover a number of different developers. The developing solution had the following composition:

Developing agent	*M*/20
Sodium Sulfite crystals	100 gms.
Sodium Carbonate crystals	54 gms.
Potassium Bromide	1 gm.
Water to make	1000 cc.

The following developers were used:

	Amount per 1000 cc.
Catechol	5.5 gms.
Adurol	7.2 gms.
Pyrogallol	6.3 gms.
p-Aminophenol	7.3 gms.
Metol	8.6 gms.
Glycin	8.4 gms.
Amidol	10.0 gms.

Development was at 15° C. The γ, t curves were plotted. The following table shows the γ values when concentration × time is constant.

TABLE XXXVIII

VALUES OF γ FOR VARIOUS DEVELOPING AGENTS WHEN CONCENTRATION × TIME IS HELD CONSTANT (Chibisoff)

Concentration	*1*	*0.5*	*0.25*	*1*	*0.5*	*0.25*	*1*	*0.5*	*0.25*	*1*	*0.5*	*0.25*	*1*	*0.5*	*0.25*
Time of development (min.)	*1*	*2*	*4*	*2*	*4*	*8*	*3*	*6*	*12*	*4*	*8*	*16*	*5*	*10*	*20*
Catechol										0.35	0.60	0.70	0.52	0.75	0.86
Pyrogallol				0.42	0.48	0.52	0.50	0.74	0.67	0.75	0.95	0.81			
Adurol				0.41	0.38	0.30	0.58	0.57	0.43	0.76	0.76	0.61			
p-Aminophenol				0.32	0.49	0.63	0.46	0.76	0.82	0.59	0.88	0.94			
Metol	0.37	0.56	0.67	0.81	0.98	1.20									
Amidol	0.39	0.60	0.43	0.76	1.12	1.04									

It is seen that γ is not independent of the concentration and that it is affected by the individual properties of the developing agents. Within limits, the action of some of the developing agents (adurol, pyrogallol, amidol) is similar to that found by Nietz and Whitaker. By interpolation on the γ, t curves, the time of development necessary to obtain a given value of γ for a given concentration is easily determined. To determine this time, it is convenient to plot the relation between the logarithm of the time and the concentration which gives a standard γ. This may be called the *iso-γ* line, and in Figure 114 are shown the iso-γ lines for the developers studied by Chibisoff. For different γ values, the iso-γ lines are approximately parallel for a given developer. From these results, the coefficient of dilution K_c may be calculated, which gives the increase in the time of development for a given decrease of concentration of the developing solution. This coefficient does not depend to any great extent on the γ but changes with the dilution. The following table shows the K_c values for the developers studied when the concentration was halved, the values being given for two different intervals:

TABLE XXXIX

Coefficient of Dilution for Various Developing Agents (Chibisoff)

Developer	Coefficient K_c *Interval of Dilution 1 : 2*	 *Interval of Dilution 2 : 4*
Catechol	1.43	1.69
Hydroquinone	1.65	. .
Pyrogallol	1.56	2.26
Adurol	2.06	2.50
p-Aminophenol	1.26	1.70
Methyl-*p*-aminophenol	1.67	1.55
Glycin	1.61	1.81
Amidol	1.32	2.28

A number of workers have studied the effect of changes in the composition of the developer. In the first place, the concentration of the developing agent itself may be considered with (1) a constant composition as regards the other components, or (2) a constant pH.

In the earlier investigations, the first of these conditions was fulfilled. In the more recent work, such as that of Reinders and

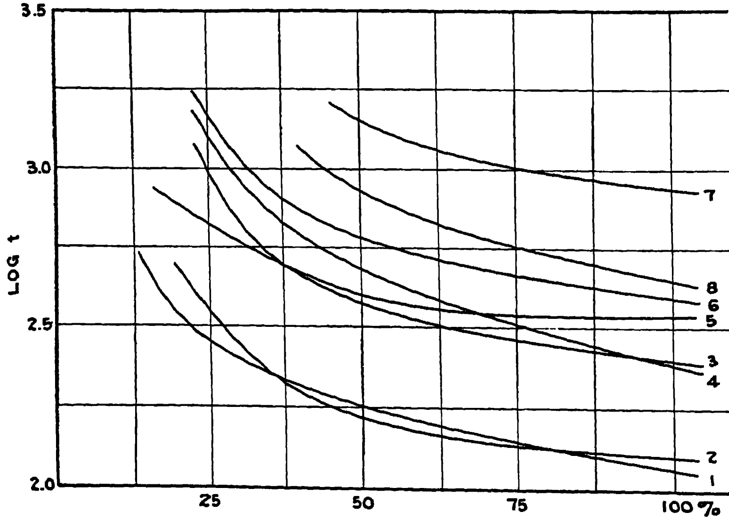


Fig. 114. Iso-γ lines for various developing agents: (1) metol; (2) amidol; (3) pyrogallol; (4) adurol; (5) paraminophenol; (6) catechol; (7) glycin; (8) hydroquinone.

Beukers,[16] the effect of pH was controlled while the concentration of the developing agent was varied. In the earlier studies in which the amount of alkali in the solution was held constant, the effect of a variation of the concentration of the developing agent was to produce a complex, irregular change in the velocity of development, as would be expected from the fact that this method of procedure involves not only a change of the developing agent but a change in the pH. Thus, with hydroquinone, the observations of Sheppard and Mees were that the rate of development increased at first with the concentration of hydroquinone, reached a maximum speed at a concentration of approximately $M/40$, and then decreased, the concentration of alkali throughout this experiment being 0.0485 N.

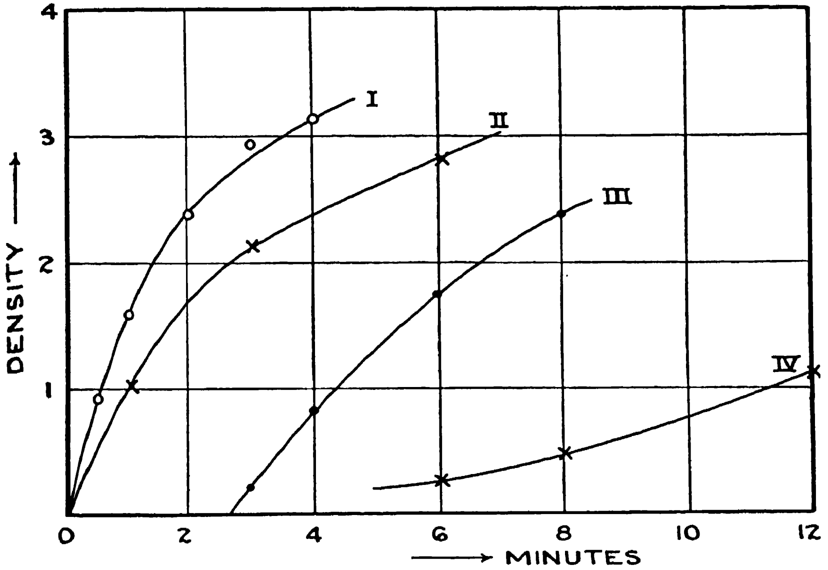


FIG. 115. Relation of the density to the time of development for two concentrations of developing agent at a pH of 9.70: I, 0.1 mol metol; II, 0.033 mol metol; III, 0.1 mol hydroquinone; IV, 0.033 mol hydroquinone.

These effects will be understood at once if the pH is considered. Thus, Reinders and Beukers measured the effect of the concentration of hydroquinone in a developer of which the pH was maintained at 9.88. From these authors is reproduced Figure 115, in which is shown the increase of density with time of development for two concentrations of metol developer and two of hydroquinone, the pH of the developing solution being 9.70 in all cases and the exposure, of course, being the same.

In the case of hydroquinone, the kinetics of the reaction throw light upon the nature of the development reaction. Thus, James,[17] working with sulfite-free hydroquinone solutions, found that the development rate varies fairly exactly with the square root of the hydroquinone concentration and with the first power of the hydroxyl-ion concentration. To interpret these results, it must be remembered that in the pH range employed (8.0–8.9), hydroquinone exists in three forms: the un-ionized, the singly ionized, and the doubly ionized. An attempt to correlate the variation in concentration of these forms of hydroquinone with the kinetics of development was successful only in the case of the divalent ion. The concentration of the latter varies as the first power of the hydroquinone concentration and the square of the hydroxyl-ion concentration. The square root of the divalent-ion concentration, therefore, varies—like the rate of development—as the square root of the hydroquinone concentration and the first power of the hydroxyl-ion concentration.

The fact that the reaction rate is related to the square root and not the first power of the divalent ion is good evidence that adsorption plays an important role in the reaction. Such a relationship is common in reactions which involve adsorption of at least one of the reactants; and it arises from the fact that the amount of material adsorbed is given to a good approximation by the expression

$$\text{amount} = kc^n,$$

where c is the concentration in solution and n is a fraction which is not uncommonly 0.5.

Such evidence as the above would, of course, not be particularly important if the kinetics could be explained logically on any other basis, but such is not the case. The results may be accepted as a confirmation of the suggestion of Sheppard and Mees that the divalent ion is the active developing agent and that, in the absence of considerable quantities of silver halide solvent, the reaction occurs while the ion is adsorbed to something, probably the silver halide itself. Under normal working conditions (pH from 9.0 to 11.0), the concentration of the divalent ion in a hydroquinone solution is quite small, and in reality a very dilute developer is being used.

Kan-Kagan [18] studied the effect of the concentration of metol holding the pH constant. In order to use a very simple developer and one which would not oxidize too rapidly, he employed a solution containing sodium sulfite, 0.127 N, and the amount of sodium carbonate to obtain a pH equal to 10.6. The amount of sulfite in this solution is sufficient to diminish oxidation to a minimum. With the highest concentrations of metol, it was necessary to use sodium hydroxide in addition to the carbonate to produce the required pH. The buffering action of the sulfite and carbonate was sufficient to prevent a change of pH through a moderate range of dilution. A change in the concentration of metol in this developer produced considerable variations in the shape of the characteristic curves, which corresponded to differences in the rate of development. The effect of the changes in concentration of the developing agent, therefore, required a com-

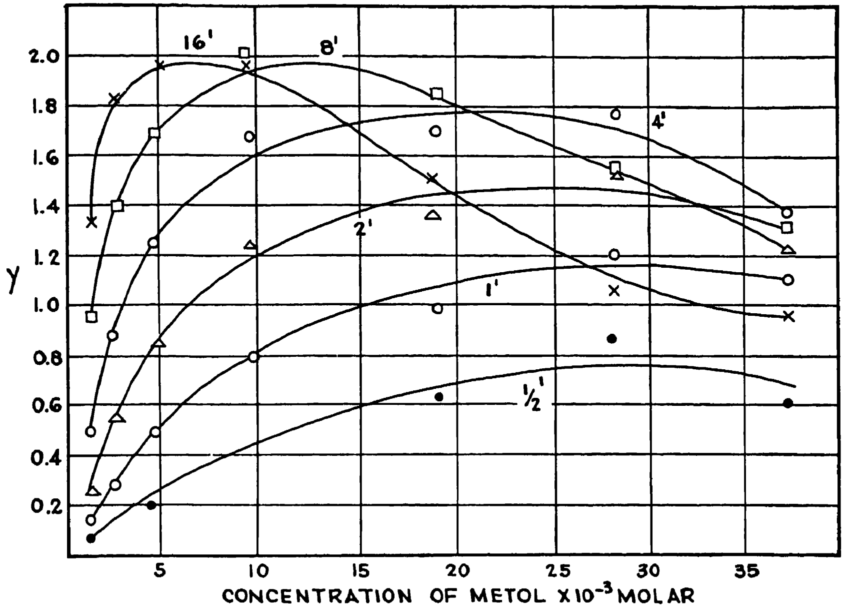


FIG. 116. Relation of γ to the concentration of metol for various times of development.

parison of the characteristic curves themselves as obtained with different times of development. From these curves, the γ's could be read, and in Figure 116 is shown the relation between γ and the concentration of metol with various times of development. The drop of γ with continued development at high concentrations is probably due to the production of fog, which is shown by the characteristic curves to have been considerable. It is probable that results of this type are valid only for the particular emulsions used, so that in work on the composition of the developer, it is necessary to specify the material employed and to repeat the work for any new material. The results given here must be considered only as summarizing the work on the subject done in the past and as indicating the lines along which experimental work should be performed.

THE EFFECT OF ALKALI IN THE DEVELOPER

In designing a formula for a developer, the determination of the pH of the solution is of primary importance. Not only must the alkali be adjusted to give the necessary pH, but the developer will be unstable unless there is present a considerable amount of buffer to maintain the alkalinity at the required level. This buffering action may generally be obtained by the use of a suitable alkali. The organic developing agents vary widely in the amount of alkali required for the operation of a satisfactory developer. The following general conclusions are drawn by Chibisoff and may be considered useful:

1. Most of the organic developing agents, especially the phenols, do not develop without alkali. Only the aromatic amino compounds with two or more amino groups show developing power under these conditions.
2. The rate of development increases with the alkalinity but this reaches a limit, after which no increase in alkali will increase the rate of development.
3. The limiting amount of alkali depends somewhat on the nature of the material.

The effect of alkali in the developer was studied in detail by Hurter and Driffield,[6] Sheppard and Mees,[2] Lumière and Seyewetz,[19] Meidinger,[20] and Sheppard and Anderson,[21] but since none of these investigators measured the pH of the solution, it was not until Reinders and Beukers[16] and Faerman and Shishkina[22] published their papers on the subject that the effect of the pH and the importance of buffering on the composition of a developer were clearly understood. Their results were confirmed in a later paper by Bürki and Ostwalt.[23]

The primary function of the alkali in a developer, especially if the developing agent is a phenol, is to produce dissociation with the liberation of ions of the developing agent in the solution. For example, in the case of hydroquinone, the dissociation follows the equation:

$$C_6H_6O_2 \rightleftharpoons C_6H_4O_2^{--} + 2H^+$$

According to Ostwald's law of dilution:

$$\frac{[C_6H_4O_2^{--}][H^+]^2}{[C_6H_6O_2]} = K;$$

that is, the concentration of the active anion is determined by the concentration of the hydrogen ions in the developing solution. In acid solution, with a high concentration of H^+ ions, the amount of $C_6H_4O_2^{--}$ anions is evidently small, and development does not take place; in alkaline solution, the rate of development depends upon the concentration of the $C_6H_4O_2^{--}$ anions; that is, on the pH of the solution.

The pH of the developing solution can be measured by several methods, such as the use of a hydrogen electrode, a glass electrode, or by colorimetry, using indicators. For laboratory work, the glass electrode is both convenient and rapid, but, for practical photography, indicators are satisfactory. Reinders and Beukers came to the conclusion that, for accurate work, the use of indicators is not sufficiently sensitive and that electrometric determinations of pH are to be preferred.

The amount of alkali needed for a definite pH depends on the nature of the developing substance and its concentration as well as that of the sodium sulfite. Table XL shows the amounts of different alkalis used in the developer to obtain pH's of 9 and 10 according to the data of Faerman and Shishkina. It is seen that the molar concentration of carbonates and hydroxides to obtain a pH of 9 is almost the same, while a considerably larger amount of carbonate than hydroxide is used to obtain a pH of 10.

If, however, developers are made up with the various alkalis, it will be found that there is some difference in behavior, notably that for the same pH and, especially, for the higher values of pH, the density obtained is greater with the carbonated than with the caustic alkalis; this must be ascribed to the buffering action of the alkali. Hydroxides do not have the buffering action shown by the salts of weak acids, such as carbonates, borates, and phosphates, because these acids have a very low degree of dissociation, and, consequently, in the presence of their anions, the hydrogen-ion concentration is low. Since the reaction of development liberates hydrogen ions, the buffering action of the alkali is of great importance. A developer with little buffering action changes its alkalinity during development, while one containing a buffer maintains its pH at a constant level.

TABLE XL

CONCENTRATIONS OF VARIOUS ALKALIS FOR GIVEN VALUES OF pH
(Faerman and Shishkina)

Alkali	*pH*	*Grams of Alkali per Liter*	*Molar Conc.*	*pH*	*Grams of Alkali per Liter*	*Molar Conc.*
K_2CO_3	9.2	1.52	0.011	10.7	27.64	0.20
Na_2CO_3	9.1	1.36	0.013	10.6	21.20	0.20
NaOH	9.1	0.33	0.008	10.6	0.63	0.016
KOH	9.1	0.67	0.012	10.8	1.36	0.024

Reinders and Beukers studied especially a hydroquinone developer containing buffers such as borax, dibasic sodium phosphate, and sodium bicarbonate. In Figure 117 is seen the relation between the density and the pH which they obtained for development times of 6 and 10 minutes. They concluded that these results were generally applicable and that both with hydroquinone and most other developers, the particular buffer used was of small importance, and that the velocity of development depended chiefly on the value of pH. An exception, however, is the use of borax with pyrocatechol and pyrogallol, with which it forms complexes.

Developing agents naturally show differences in their response to differences in the value of pH. This is shown in Figure 118.

The aminophenols are not very sensitive to differences in the pH of the solution, even in the case of glycin, but the difference is particularly marked with developers such as pyrogallol and hydroquinone, both of which have very definite and limited ranges of pH through which they are suitable for use as developers. Figures 119 *A*, *B*, and *C* show the curves of density plotted against time of development for different values of pH in hydroquinone, metol, and *p*-aminophenol developers.

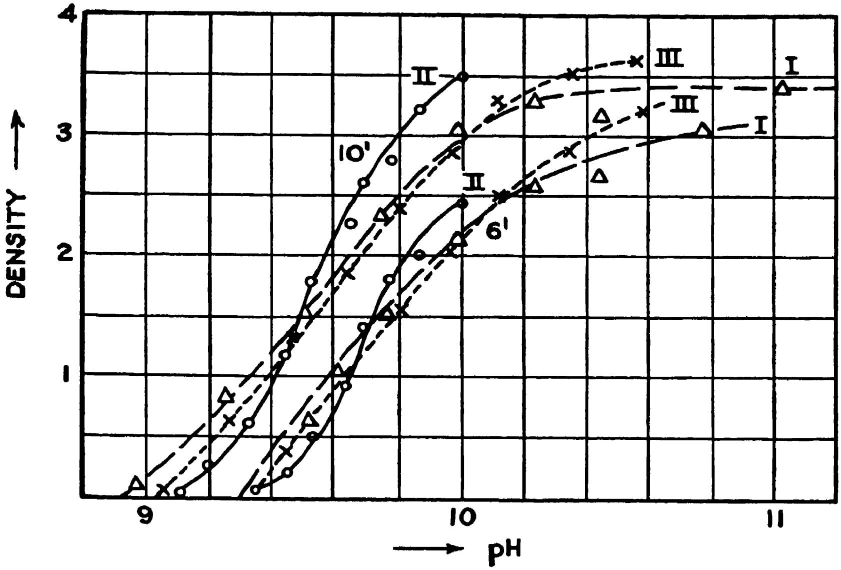


FIG. 117. Relation between density and pH for development times of 6 and 10 minutes: I, 0.1 mol disodium hydrogen phosphate buffer; II, 0.1 mol borax buffer; III, 0.1 mol bicarbonate buffer.

It is seen that the range of pH usable in the case of hydroquinone is very small and is very much greater in the case of *p*-aminophenol, while metol falls between the two. In the case of hydroquinone only, there is a very marked induction period. Reinders and Beukers consider that for a practical developer, (1) the developing solution must be arranged to have as great a buffering action as possible; (2) the sensitivity of the developer to a change of pH should be as small as possible. They also conclude that it is more convenient to use developing solutions with low pH values.

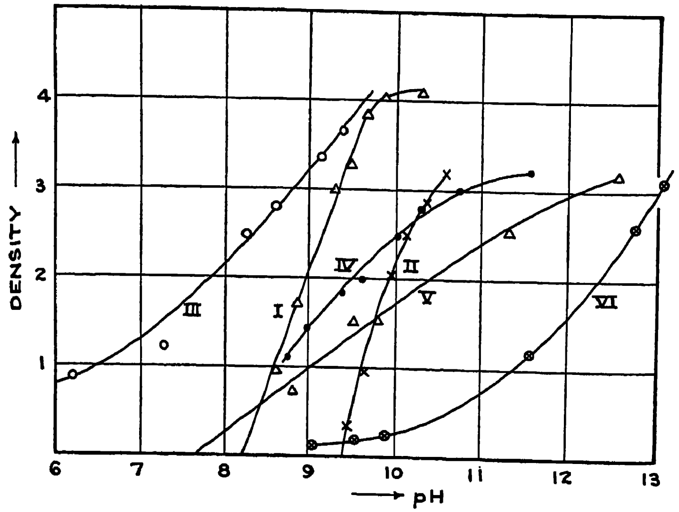


FIG. 118. Relation between density and pH for various developing agents:

I. 0.1 mol pyrogallol 0.1 mol sodium bicarbonate
II. 0.1 “ hydroquinone 0.1 “ “ “
III. 0.1 “ metol 0.1 “ borax
IV. 0.033 “ *p*-aminophenol 0.05 “ “
V. 0.1 “ glycin 0.05 “ “
VI. 0.05 “ *p*-phenylenediamine 0.05 “ “

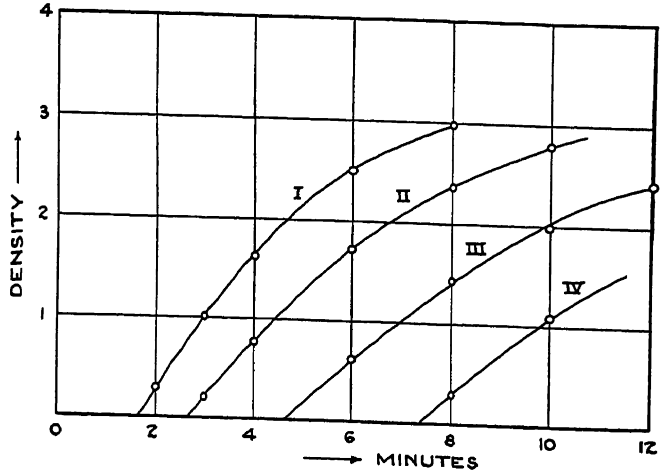


FIG. 119A. *D*, *t* curves for various values of pH:

I. pH = 9.95
II. pH = 9.70
III. pH = 9.45
IV. pH = 9.20

Developer: 0.1 mol hydroquinone; 0.05 mol borax.

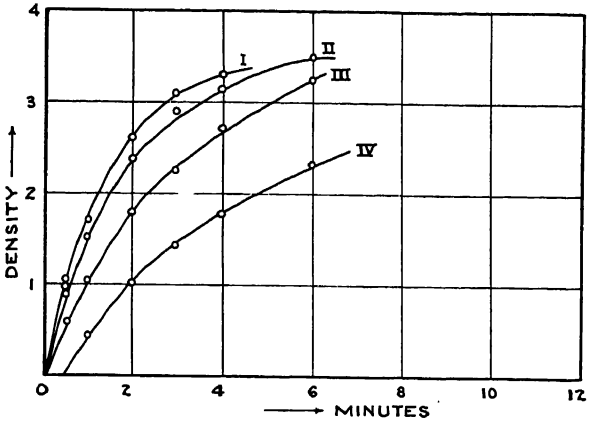


FIG. 119B. *D, t* curves for various values of pH:

I. pH = 9.95
II. pH = 9.70
III. pH = 8.95
IV. pH = 7.95
Developer: 0.1 mol metol; 0.05 mol borax.

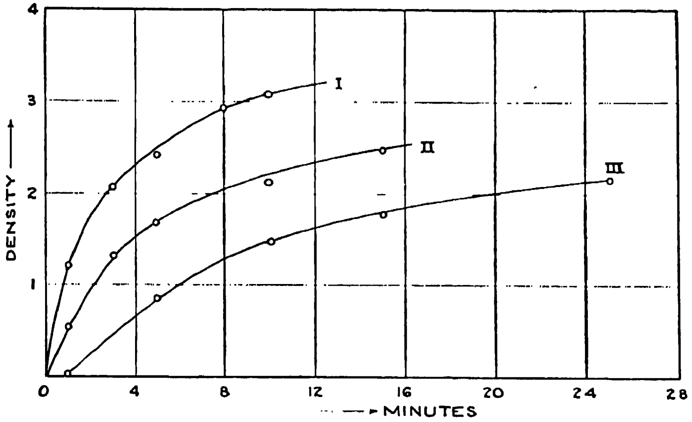


FIG. 119C. *D, t* curves for various values of pH:

I. pH = 11.82
II. pH = 9.67
III. pH = 8.73
Developer: *p*-aminophenol-borax.

THE TEMPERATURE COEFFICIENT OF DEVELOPMENT

The velocity of development is greatly affected by the temperature. In practice, it must be accurately controlled, and, from the theoretical standpoint, any consideration of the mechanism of development must take into account the temperature coefficient. Sheppard and Mees[24] point out that the ratio of the velocities for a change in temperature of 10° C. is of value as a criterion in heterogeneous reactions. For chemical reactions in homogeneous solution, the value of the temperature coefficient is generally about 2 to 3, while for diffusion processes a value of about 1.5 would be expected. They give the following table, from which it is seen that the temperature coefficient varies very greatly with different developing agents and also varies with the type of material developed. In any case, the values are higher than those which would be expected if the velocity were conditioned by diffusion. Sheppard and Mees conclude that a high temperature coefficient in development does not necessarily imply that the velocity is that of the chemical reaction.

TABLE XLI

TEMPERATURE COEFFICIENTS OF DEVELOPERS (Sheppard and Mees)

Reducer	*Emulsion A*	*B*	*C*
Ferro-oxalate	1.60	1.90	1.70
Ferrous Citrate	1.52	..	..
Ferrous Fluoride	1.54	..	..
Hydroxylamine	..	..	2.00
Hydroquinone	..	2.20	2.80
p-Aminophenol	..	..	1.50
Metol	..	..	1.25
Catechol	..	2.80	..

A study of the effect of temperature upon the time of development required to produce a given γ was carried out by Ferguson and Howard.[25] They suggest that if the velocity at, for example, 10° C. is represented by k, the velocity at 11° C. may be expressed by kb, and at $10° + x°$, by kb^x. If the temperature coefficient for 10° is K_T and b is the temperature coefficient for a single degree, then $K_T = b^{10}$. This relation does not give a straight line for the time of development plotted against the temperature, but Stokes[26] pointed out that such a straight line would be obtained if the logarithm of the time were plotted against the temperature. The validity of this conclusion was studied by Chibisoff and his associates. They determined the γ, t curves for a number of different developers at three temperatures—10°, 15°, and 25° C.—and from these constructed curves showing the relation between the logarithm of the time

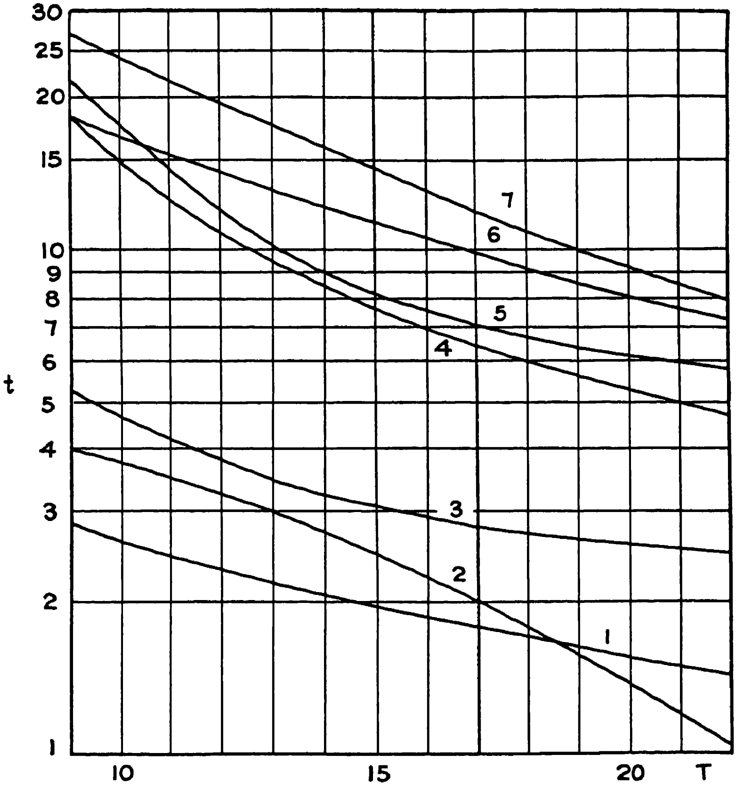


FIG. 120. Iso-γ lines (temperature plotted against log t for various developers): 1, amidol; 2, metol; 3, pyrogallol; 4, p-aminophenol; 5, catechol; 6, hydroquinone; 7, glycin.

and the temperature for constant γ. These are shown in Figure 120. It is seen that the relation between $\log t$ and the temperature is not generally linear for a wide range of temperatures but that, to a first approximation for a range of 5° to 10°, $\log t = KT + Y$. In the practical application of the temperature coefficient to the calculation of the time of development at different temperatures, the question arises as to whether the temperature coefficient is dependent upon the photographic material used. This was found to be a fact by Sheppard and Mees, a result confirmed in a note by Watkins[27] published in 1910. Ferguson[25] found that the temperature coefficient varied with the material. Thus, on a group of plates, he found temperature coefficients as low as 1.55 and as high as 2.01 for the standard pyro-soda developer which he used, but he also found that the addition of bromide to the developer increased the temperature coefficient very noticeably in the case of those materials which had a low temperature coefficient in the absence of bromide. Thus, in the case of an Imperial Ordinary plate in the absence of bromide, the temperature coefficient was 1.71, whereas the addition of one part in one thousand of potassium bromide raised the temperature coefficient to 2.02. With this bromided developer, Ferguson found practically no change in the temperature coefficient with different materials. The developer used had the following composition:

Pyrogallol	4 gms.
Sodium Carbonate crystals	20 gms.
Sodium Sulfite crystals	20 gms.
Potassium Bromide	10 gms.
Water to make	1 liter

This developer was found to have a temperature coefficient of approximately 2.0 for all the materials tested.

THE DEVELOPMENT OF FOG

When a developer acts upon an emulsion layer, some grains which have *not* been exposed to light are reduced to metallic silver. The density obtained in the unexposed portions of the image is known as *fog*. The production of fog may be ascribed to the emulsion or to the developer; that is, some emulsions show much greater fog than others and some developers have a greater tendency than others to produce fog.

In practical photography, fog is invariably regarded as a disadvantage, and, as will be seen, the origins of fog are complex. Fog arising primarily from the emulsion may be due either to grains which have been exposed to light accidentally or, more often, to grains nucleated during the preparation of the material otherwise than by light. The developer itself, however, may produce fog in grains which appear to be normal, and the origin of this fog can be traced to certain definite chemical effects produced by the developer.

Omitting any discussion on the development of grains which have been exposed to light, a phenomenon which does not differ from that of the normal image, silver bromide grains may become developable during the preparation of the emulsion. It must be remembered that silver halide precipitated in the dark but in the absence of excess bromide and of gelatin is easily reduced by the developer to metallic silver. This reduction is greatly hindered by excess bromide and by gelatin, which protect the grain from reduction unless a nucleus has been produced upon it (Chapter III). The nucleus may be produced in the same way as the sensitizing of the grains; that is, a developable nucleus may possibly be an exaggerated sensitivity speck, since it is well known that continued treatment with sulfur sensitizers of the type which produce enhanced sensitivity in the emulsion may eventually make the emulsion develop fog.

It is possible also that grains become developable by other means than those which produce the normal sensitivity specks; if an emulsion is heated for a long time, it will cease to increase in sensitivity, but the fog produced in development will grow and eventually become very great. This production of fog is associated generally with an actual reduction of sensitivity. The loss of sensitivity may, of course, arise from the production of numerous sensitivity specks, the competition of which for the silver produced by exposure to light reduces the effective concentration of the latent image, as suggested by Sheppard; on the other hand, developability upon long-continued digestion may be due to the production of reduced silver on the surface of the grain. Chibisoff and Mikhailova [28] found that very long times of digestion produce a decrease in the amount of fog compared with that produced by moderately long times, and they regard this decrease as comparable to the phenomenon of solarization. The shape of the curves showing the relation between the fog and the time of digestion is dependent upon the size of the grains but, apparently, does not vary with the gelatin used (Figure 121). The authors conclude definitely that the nuclei which induce fog upon development are identical with those produced by light.

Photographic materials which are initially free from fog develop fog when they are kept for a long time and, especially, when they are kept at a high temperature. The tendency of an emulsion to develop fog either upon immediate development or after keeping is a very disadvantageous property, and methods for minimizing it are carefully studied by the emulsion maker. Even materials which show a minimum of fog with normal development develop fog in some circumstances, and there are developers which produce development of the unexposed grains.

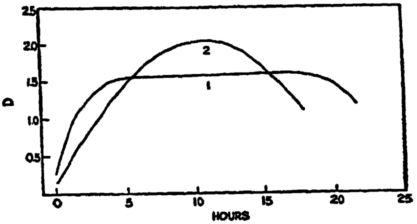


FIG.121. Curves showing relations between the fog and the time of digestion of the emulsion: 1, fine-grain emulsions; 2, coarse-grain emulsions.

The quantitative study of fog produced by development is very difficult owing to the complexity of the phenomenon. It is desirable to regard development fog as characteristically different from the density produced in an exposed image and as produced possibly by a different mechanism. In the presence of a latent image, however, it is usually not possible to determine whether density has been produced as fog or as image. Furthermore, the amount of fog in a given area must decrease with increasing latent image, because some of the grains which might have developed as fog develop as image. Some distinction can be made because, as a general rule, fog can be diminished by chemical additions to the developer, such as bromide and the so-called *antifoggants*, which to a much less degree affect the development of the latent image. Moreover, the temperature coefficient of the growth of fog and the covering power of the deposit are characteristics which distinguish fog from an image.

In the same emulsion the optical density of fog does not usually bear the same relation to the mass of the silver as the image does. It is not unusual, especially when silver halide solvents are present in the developer, to obtain fog of extremely low covering power, often whitish in color and slightly brown by transmitted light. Such fog may occasionally represent half the developable silver of the emulsion and yet not have a density higher than 0.2 by transmitted light[29] (Chapter V, p. 231).

By studying the rate of growth of fog compared with that of the exposed image, Nietz came to the conclusion that the development of the image and of fog does not follow the same law, the velocity functions being different. In his experiments, the normal development process for the image was found to be described by the velocity equation (III) given on p. 432, while equation (II) fitted his measurements of the growth of fog much better. Thus, he found that the velocity of development for the image was

$$\frac{dD}{dt} = \frac{k}{t}(D_\infty - D),$$

and for fog it was

$$\frac{dD}{dt} = k(D_\infty - D).$$

In these experiments, Nietz found that fogging proceeds to a definite limit, as the image does, and he was able to calculate values for D_∞, k, and t_0 for the production of fog. He found that the value of D_∞ for fog depended very much upon the developing agent and gave the following table for various developers:

TABLE XLII

Classification of Developers According to Maximum Fog (Nietz)

	(D_∞) *Fog*	(D_∞) *Image*	*F after 20 minutes*
p-Amino-metacresol	2.60	4.00	2.51
Toluhydroquinone	2.45	4.40	2.34
Hydroquinone	1.50	3.80	1.32
Diaminophenol + alkali	1.30	4.20	1.20
Monomethyl-*p*-aminophenol	1.30	3.60	.90
Pyrogallol	1.30	4.00	.88
Methyl-*p*-amino-orthocresol	1.20	4.00	1.03
Dibromhydroquinone	1.00	3.80	.76
Dimethyl-*p*-aminophenol	.99	3.20	.70
Dichlorhydroquinone	.75	3.60	.49
Diaminophenol, no alkali	.70	3.60	.62
p-Aminophenol	.70	4.20	.44
p-Amino-orthocresol	.65	3.80	.57
Phenylhydrazine, no alkali	.65	3.50	.18
Chlorhydroquinone	.60	4.00	.55
Bromhydroquinone	.60	3.80	.55
Ferro-oxalate	.43	3.10	.38
Catechol	.40	3.60	.38
Edinol	.30	3.60	.27
Duratol	fog negligible	2.40	.05
p-Phenylenediamine, no alkali	fog negligible	1.70	.05

If this table is compared with Nietz' figures for the bromide potential of the developing agents, it will be seen that there is no relation between fogging power and the bromide potential.

The quantitative statement of the fogging power of a developer involves much difficulty. In their early work on the subject, Mees and Piper[30] found that fog increases at an approximately uniform rate and defined the fogging power of the developer as the density of the fog after 10 minutes' development. At the same time, they determined the velocity constant of development for the image as the constant k measured in the usual way. They then expressed the relative fogging power ϕ as equal to $\frac{F}{k}$.

As has already been stated, Nietz found that fog does not increase linearly with time but follows an exponential law of the same general type as that applying to the image, but, nevertheless he found it convenient to state the fog in terms of that produced after 20 minutes of development; that is, he classified developers primarily in terms of the maximum fog density they would produce.

Shiberstoff and Bukin[10b] express the fogging action of developers as $\frac{dF}{dt} = \delta$ and give the following table for the values of δ for a number of different developing agents at several temperatures. The developing formula used was:

Developing agent	$M/20$
Sodium Carbonate, anhydrous	25 gms.
Sodium Sulfite, crystallized	50 gms.
Water to	1 liter

TABLE XLIII

THE FOGGING POWER (INITIAL VALUE OF dF/dt) FOR VARIOUS DEVELOPERS (Shiberstoff and Bukin)

Developers	*δ at 15° C.*	*δ at 20° C.*	*δ at 25° C.*
p-Phenylenediamine	0.06	0.12	..
Glycin	0.07	0.14	0.28
p-Aminophenol	0.09	0.14	0.36
Catechol	0.09	0.16	0.32
Bromhydroquinone	0.25	0.41	0.80
Eikonogen	0.36	0.72	1.13
Chlorhydroquinone	0.38	0.58	1.11
Metol	0.38	0.63	1.14
Pyrogallol	0.40	0.63	1.12
Hydroquinone	0.41	0.86	1.22
Metoquinone	0.50	0.93	1.52

This table suggests that the developers may be divided into two groups, according to their fogging action: a group of developers having low fogging action, including *p*-phenylenediamine, glycin, and *p*-aminophenol, and a group having high fogging action, which in the table begins with eikonogen.

Inasmuch as developers are used in practice to produce an image in the exposed material, the significant factor is the ratio of the rate of production of fog to that of the image. Shiberstoff assumed that he could write

$$V_i = \frac{k_1}{t(D = 1.5)}$$

for the rate of development of the image and

$$V_f = \frac{k_2}{t(D_f = 0.3)}$$

for the production of fog and expressed the degree of selective action of the developer on the image in preference to fog as

$$U = \frac{V_i}{V_f} = K\frac{t(D_f = 0.3)}{t(D = 1.5)}.$$

Using this formula, he gives the following table for the selectivity of developers at three different temperatures, the composition of the solution being that given on p. 436, *K* being given

TABLE XLIV

THE SELECTIVITY OF ACTION FOR VARIOUS DEVELOPERS (Shiberstoff)

Developer	*U at 15° C.*	*U at 20° C.*	*U at 25° C.*
p-Aminophenol	500	500	250
Catechol	267	227	191
Glycin	259	210	150
Metol	240	180	200
Metoquinone	182	172	136
Pyrogallol	200	136	100
Bromhydroquinone	159	131	95
Chlorhydroquinone	186	123	106
Eikonogen	150	113	106
Hydroquinone	93	75	50

the value 100 and the optical density of the image measured for a fixed exposure. It is seen that the selectivity decreases with an increase of temperature because the rate of growth of fog increases more rapidly with temperature than that of the image. This supports Nietz' view that the mechanisms of development for the exposed image and for the production of fog are different.

The fogging power of developers discussed up to this point is what may be termed the *normal* fogging power—that due either to nucleation of the grains of the emulsion or to the action of the developer in breaking down the resistance to reduction of the silver bromide grain—but fog can be produced in other ways during development. A number of substances will produce severe fog if added to a developer. Many of these contain sulfur. Thus, thiocarbamide is an extremely powerful fogging agent in a developer, so powerful, in fact, that positive images can be produced from an exposed film in a developer containing thiocarbamide. This was discovered by Waterhouse,[31] and the mechanism of the reversal has been studied by Rawling.[32] There is little doubt that the cause of the reversal is the great sensitivity to the presence of free bromide ions shown by the nucleation by thiocarbamide. When the exposed material is first immersed in the developer, the more heavily exposed portions develop to produce a faint image and, at the same time, produce *in situ* free bromide ions. Meanwhile, the thiocarbamide reacts with the silver bromide, forming a complex addition product. With dilute thiocarbamide solutions, the complex formed is insoluble and remains on the surface of the silver bromide. In the presence of the alkali of the developer, the thiocarbamide complex decomposes and forms silver sulfide nuclei on the grains, which makes them developable, so that they develop very rapidly indeed.

Inasmuch as the decomposition of the thiocarbamide complex is hindered by the presence of small quantities of soluble bromide, the bromide ions formed by the initial development of the latent image prevent the nucleation of grains in the region where the initial development occurred. Thus, a positive is obtained in the highlights in which there is present a faint image owing to the initial development of the original exposure.

It is notable that the silver deposited in thiocarbamide development is often colored, its structure in that case appearing quite different from that of the image. However, Rawling mentions specifically that if small amounts of thiocarbamide were used, he found the image to be of the ordinary black type and to consist of developed grains.

Mees and Piper found that a similar phenomenon was produced in a hydroquinone developer by very low concentrations of sulfite. In one set of experiments, the maximum fogging power was produced at a concentration of $M/160$ (cf. Figure 122 in which the fog, F, and the relative fogging power, ϕ, are plotted). Under the proper conditions, they were able with this developer to produce results parallel to those obtained with thiocarbamide. It seems possible that such low concentrations of sulfite may result in the production of some sulfide.

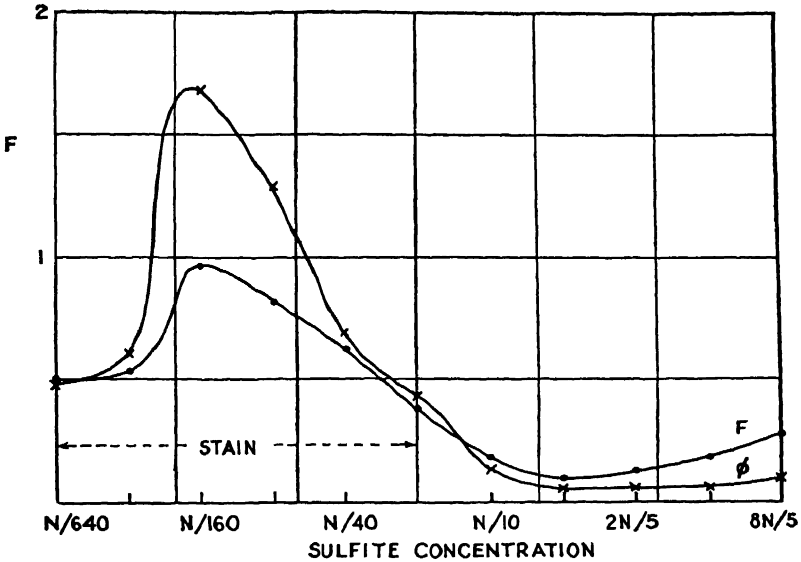


FIG. 122. Relation between the fogging power and the concentration of sulfite in a hydroquinone developer.

Fogging in development can be produced not only by sulfur compounds, which cause nucleation of the silver bromide, but by the aerial oxidation of the developer. This is particularly true in the case of hydroquinone. In a hydroquinone developer containing no sulfite, very bad fogging will be observed at the surface of the solution if a piece of unexposed film is introduced so that it is not completely immersed. The surface layer will fog the emulsion very strongly, and streaks of fog will run down onto the surface of the film immersed in the developer.

This oxidation fog presents serious problems, and the practical aspects of the matter were studied in detail by Dundon and Crabtree.[33] *Oxidation fog*, or *aerial fog*, as it is sometimes called, is greatly increased in the presence of copper. On the other hand, the desensitizing dyes such as pinakryptol green or phenosafranine in very dilute solution prevent aerial fog. Two parts per million in the developer are sufficient in most cases to remove the fog unless it is very severe owing to the presence of considerable quantities of copper.

The origin of oxidation fog is very obscure, but work on the autoxidation of developers by James and Weissberger [34] shows that, in the case of duro-hydroquinone, hydrogen peroxide can be isolated as a product of aerial oxidation, and, with hydroquinone itself, hydrogen peroxide is formed and at once reacts with the quinone. Since very small amounts of peroxide can make silver bromide completely developable, it may be concluded that oxidation fog is due to the production of hydrogen peroxide.

An alternative hypothesis for aerial fog is that due to Fuchs,[35] according to which it is assumed that oxidation of the developing agent by the air gives rise to chemiluminescence, which fogs by light action. Fuchs attempted to explain by the same mechanism many other kinds of chemical fog, such as those due to acids and oxidizing agents. It appears unlikely that his theory holds for any of them. The chief support of the view comes from the fact that all such types of fog may be prevented by the proper use of desensitizers.

Still another type of fog demands notice although with modern methods of handling and materials it is not as prevalent as formerly. This is known as *dichroic fog* because it is a different color by transmitted than by reflected light. It consists almost entirely of metallic silver deposited in the gelatin by the action of the developer on silver halides which have been dissolved from the emulsion by silver halide solvents in the developing bath. Any change in a developer formula which tends to increase its halide solvent properties without lessening its ability to reduce silver halide increases the tendency to deposit colloidal silver.

Dichroic fog is frequently so confined to the surface that it may be wiped off before the film is dried. After drying, it can usually be removed by a brief rinse in a permanganate bath followed by bisulfite treatment and thorough washing. The causes and prevention of dichroic fog are discussed extensively by Lumière and Seyewetz.[36]

ANTIFOGGANTS

To satisfy the requirement for high-quality results even under adverse conditions, as when exposures are at a minimum and development is prolonged, chemical addition agents, known as *antifoggants*, are employed to restrain the production of fog. They may be added to the developer or the emulsion.

Soluble bromide is one of the most common antifogging compounds. Its use in developers dates from the earliest days of photography.[37] It is frequently assumed to act through the mass action law and decrease development by acceleration of the opposing formation of silver bromide, thus retarding the reduction reaction brought about by the developing agent. For the kinetics of the development of a latent image, this action has already been discussed in an earlier part of this chapter. It is shown that there is some evidence that the action of bromides is also associated with the surface adsorption equilibrium at the grain surface. These apparent adsorption effects seem even more pronounced in the case of fog, the appearance of which is frequently so postponed by bromides that development of the latent image reaches the desired stage before fog is visible. The shape of the characteristic curve for such a case is usually different from that to be expected if the bromide had no effect on the latent-image development.

Sheppard and Hudson[38] in 1927 first reported that thioanilides restrain the production of fog. The thioanilides have the structure R·CS·NH·Ph or, according to Sheppard, more probably, R·C(SH) : NPh. They form addition agents with silver halides, as do the thiocarbamides, but the complex formation appears to take place through the *nitrogen* atom and not through the *sulfur* atom. The complexes are stable in alkali solution, and, consequently, the thioanilides do not act as sulfur sensitizers but as restrainers of development and fog inhibitors.

Trivelli and Jensen,[39] after noting the action of the thioanilides, investigated the effects of compounds previously patented as antifoggants in emulsions.[40] They chose 6-nitrobenzimidazole as the most interesting of the series and showed that in a concentration of one part in 25,000, this compound, compared with a concentration of potassium bromide giving the same fog restraint, causes considerably less loss of image density. It is, accordingly, a better restrainer for fog and gives a greater ratio of image to fog density than bromide. Benzotriazole and 5-nitroindazole are very similar in behavior to nitrobenzimidazole and can be used in the same way.

A large number of organic compounds act as antifoggants if added to emulsions and are classified in the patent literature as "antifoggants," "fog inhibitors," and "stabilizers." They include alicyclic amines, pyrazoles, pyrimidines, among others. That most effective in a given emulsion must be found by trial.

The explanation given by Sheppard for the action of the thioanilides may probably be extended to cover the action of all these compounds. Sheppard finds that they form complexes with silver bromide, and he believes that their effect in preventing fogging and restraining development can be explained by the view that the complex silver compound is first formed at the interface between the sensitizing specks of silver sulfide and the silver bromide. The silver halide in the immediate neighborhood of sensitizing nuclei must be regarded as especially reactive since it is assumed that the reduction to silver tends to commence at the interfaces. Following the same argument, the silver halide close to the nuclei and, especially, to large nuclei such as are assumed to produce fog would be still more reactive, and compounds from bodies such as the thioanilides would produce at this point a layer of irreducible silver compound which would tend to insulate the nuclei and prevent development. In confirmation of this, Sheppard found that for an emulsion oversensitized with allyl thiocarbamide, to the point where it tended to produce fog, treatment with thioacetanilide diminished the fog and then reduced sensitivity as the treatment was increased. The action of such antisensitizing and antifogging agents is, therefore, probably not altogether different from that of soluble bromides, since it may be supposed that these tend to be preferentially absorbed to the silver halide in the neighborhood of the fogging and sensitizing nuclei.

THE PRODUCTION OF GRAININESS IN DEVELOPMENT

It is necessary to distinguish between the size of the particles of silver of which the image is composed and the graininess, or nonuniformity of distribution, of these grains. In very few processes do the individual grains play an important part, but, if a photographic image is moderately magnified, the lack of uniformity of the deposit will become objectionable unless special preventive methods are used.

The measurement and specification of graininess are discussed in Chapter XXI, which deals with the physics of the image. Only the various means employed to diminish graininess in development are considered here.

Four general methods of producing fine grain are distinguishable:

1. Development to low γ.
2. Development in solutions of low or moderate activity containing silver halide solvents.
3. Development with *p*-phenylenediamine or its derivatives.
4. Physical development.

1. The uniformity of the deposit appears to be improved by the dilution of the developer. For the most part, however, this is only an apparent improvement and arises from the fact that development is not usually carried as far as by the stronger baths. If an emulsion carrying a latent image is placed in a developer, the reaction starts at discrete points on the grains. All development centers do not react at the same time, but, in general, as the reaction proceeds, the size of each increases. After a short time in a powerful developer, many of these centers coalesce, and complete reduction is effected for a considerable proportion of exposed grains. This necessarily decreases the number of discrete particles of silver composing an image. While there is no known direct correlation between the size and number of grains and the graininess of the deposit, the heterogeneity due to the chance distribution of a greater number of smaller grains is evidently lower than that of a smaller number

of larger grains; in other words, a large number of small grains distributed at random have less interspacing than larger ones fewer in number. Accordingly, development terminated at an early stage results in less graininess than development carried nearly to completion. Crabtree and Schwingel's [41] curves show that the degree of development has more influence on the graininess of negative than positive materials, and it is now standard practice to develop motion-picture negatives to lower γ than the positive, both for the original and duplicates. The fact that many workers have not realized that graininess varies according to the extent of development has created a copious controversial literature on graininess.

2. With the exception of agents of the *p*-phenylenediamine series and possibly *o*-aminophenol, the differences in graininess produced by various developing agents are rather small if development is carried out to equal γ's. This is not true, however, if silver halide solvents are added to the developer, but these usually cause a loss of emulsion speed.

Typical silver halide solvents include sodium sulfite,[42] ammonium chloride [43] and organic amines, sodium thiosulfate,[44] and thiocyanates.[45] Possibly the most typical developer formula containing silver halide solvents is Kodak DK-20,[45] a metol formula containing two silver halide solvents—sodium (or potassium) thiocyanate and the less active sodium sulfite. Developers containing large quantities of sodium sulfite as the only solvent are very popular but give only a slight reduction in graininess. To be effective, silver halide solvents must be used in developers of low activity. Lüppo-Cramer [46] found that silver halide solvents retard normal chemical development and accelerate physical development and so produce fine-grained images. He points out that the restraint of chemical development is brought about by the action of the solvent on the latent image, while physical development is accelerated by the increased availability of soluble silver halide complexes.

3 The outstanding development agent which, by itself, gives fine-grained images is *p*-phenylenediamine, as pointed out originally by Lumière and Seyewetz.[47] The exact reason for its action is not known, but it is similar in many respects to that of solutions containing the more active silver halide solvents. It

has a strong solvent action for the halide (Lumière and Seyewetz [43]), is adsorbed to the grains, and is strongly physical in its development action. It must be used in developers of even lower activity than are required with silver halide solvents, although certain of its derivatives may be used in developers of moderate activity. Unfortunately, *p*-phenylenediamine and nearly all of its derivatives tend to produce severe dermatitis with prolonged use.

In a microscopical study of the development of silver halide emulsion in its relation to graininess (Chapter XXI, p. 834), Loveland* sought to avoid the errors which arise from observations on single-layer microscopical preparations interpreted in terms of an emulsion layer of normal thickness. He examined both single-layer and multi-layer preparations which had received controlled exposures and development and in this way studied many different combinations of emulsion and developer under the conditions used in practice.

Loveland's results show that pure silver bromide crystals do not change in shape if developed to metallic silver in a hydroquinone developer of very low sulfite action and, therefore, without solvent action (single-layer and multilayer coatings behaved similarly). He considers this typical of chemical development and concludes that, in crystals in the form of thin triangular or hexagonal plates, development starts at one or more points on an acute edge, which is quickly converted to metallic silver. Obtuse edges are the next to be attacked, after which the development spreads inward. If a pure silver bromide emulsion was developed in a hydroquinone developer having the normal concentration of 75 grams of sodium sulfite per liter, the nondeveloped grains were partly dissolved by the sulfite from the single-layer coatings but not from the multilayer ones. In addition, the developed grains were no longer exact pseudomorphs of the original silver bromide crystals but had somewhat ragged edges. If the same pure silver bromide emulsion was developed in a metol-hydroquinone developer of normal sulfite concentration, an even greater change in shape was obtained; oblong projections appeared on the developed grains, and there was some increase in graininess of the developed image.

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* R. P. Loveland, private communication.

Emulsions containing silver iodide with the silver bromide behaved differently from those of pure silver bromide; for example, a low-iodide emulsion developed in hydroquinone showed as much graininess as the pure bromide in metol-hydroquinone. The grains of the low-iodide emulsion were more distorted than

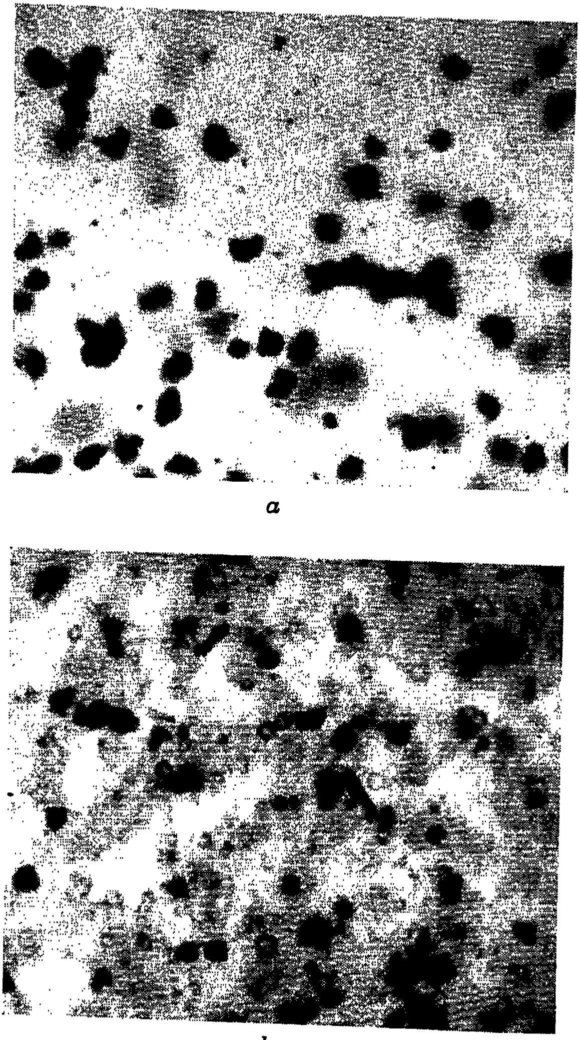

FIG. 123. Silver grains from a pure bromide emulsion developed (*a*) in a fine-grain developer containing thiocyanate; (*b*) in a hydroquinone developer. ×2500.

the pure bromide ones: triangular crystals distorted on two sides only. The grains of high-iodide emulsions, even if developed in a low-sulfite hydroquinone developer, grew many projections, which caused development to spread to contiguous grains. This gave rise to a clumping effect in the silver image. With high-sulfite hydroquinone, the solvent action was irregular, as if the silver iodide were irregularly distributed throughout the individual crystals.

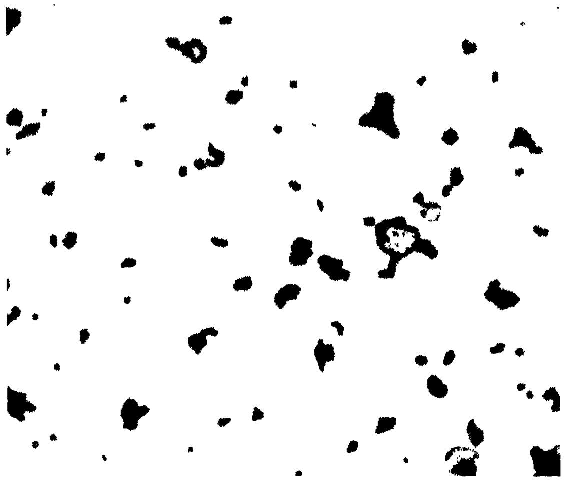

FIG. 124. Silver grains from a high-iodide emulsion developed in a solution containing thiocyanate. ×2500.

Loveland also studied the effect of adding silver halide solvents to the developer. With Kodak DK-20 developer containing thiocyanate, the solvent action was very marked on grains which did not develop. It was excessive with pure bromide emulsions, and many long streaks of silver were formed with both single-layer and multilayer coatings. In the preliminary phase of development, some grains were completely reduced, and the rest went into solution. The subsequent and main part of the development was by deposition of silver on the silver grains produced in the first phase. Figures 123*a* and 123*b* are a comparison of multilayer preparations of a pure bromide emulsion developed to equal contrast in a thiocyanate fine-grain developer and hydroquinone developer, respectively; neither was fixed except by the solvent action of the developer itself. It is seen that the thiocyanate developer increased the size of the grain of the pure silver bromide emulsion, and instead of exceptionally small grains being produced, they are actually larger than those produced by an ordinary hydroquinone developer. Loveland considers that this is because the development of the pure silver bromide starts without an appreciable induction period, so that by the time the solvent action of the developer becomes pronounced, there are plenty of silver grains on which the silver can be deposited. With a high-iodide emulsion, a thiocyanate developer does give a fine grain, because the retarded development provides an induction period so that the dissolved silver halide has time to diffuse even into the bulk of the developer before the silver is deposited. The action of a thiocyanate fine-grain developer upon such an emulsion was almost entirely physical in character; development started from one or more centers on each grain and formed protuberances (Figure 124). With heavy exposures, development centers occurred equally on large and small crystals—perhaps even more frequently on the small crystals.

With developers containing *p*-phenylenediamine, longer exposure increased the number and decreased the size of developed silver particles. The top layer of the multilayer high-iodide plates after development contained a great many very small particles of silver, showing that the silver ions traveled some distance before reduction to silver.

Loveland's work emphasizes the influence of the relative induction periods and rates of solution and reduction of the silver halide on the physical appearance and graininess of the developed image.

4. True physical development of the post-fixation type apparently produces very low graininess at the expense of a large loss of emulsion speed. In spite of strong claims for pre-fixation physical development,[48] there is some doubt from comparisons at equal γ's whether on commercial materials this system produces any real reduction in graininess.

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CHAPTER XII

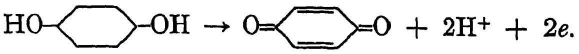
THE FREE ENERGY AND OXIDATION–REDUCTION POTENTIALS OF DEVELOPERS

The electrons which take part in the fundamental reaction of photographic development,

$$e + Ag^+ \rightarrow Ag, \qquad (1)$$

are provided by the developing agent, *e.g.*,

$$Fe^{++} \rightarrow Fe^{+++} + e, \quad \text{and} \qquad (2)$$



(3)

It has been pointed out in the preceding chapters that the discrimination between exposed and unexposed silver halide grains is the result of differences in reaction rates. Therefore, the latent image and the reduced silver play the role of initiators or catalysts for the process

$$\text{reduced state} + Ag^+ \rightarrow Ag + \text{oxidized state}. \qquad (4)$$

The free energy change, *i.e.*, the faculty of doing work, of the reduction of exposed and of unexposed grains by one and the same reducing solution can be treated as if it were identical, because any difference could not exceed the energy supplied by the exposure. (It might be argued, but it does not appear likely, that this minute difference is important for the initiation of development, *e.g.*, by a differentiation in the heat of adsorption of developer onto exposed and unexposed grains.) On the other hand, the free energy change of the process (4) varies with the reducing solutions. No general statement can be made as to how this variation influences the capacity of reducing solutions to act as developers. A theory which might link the thermodynamic properties of chemical substances and the kinetics of their reactions is still in its very early stages and does not warrant predictions concerning the complicated systems under consideration. The free energy change of the processes exemplified by equations (2) and (3) plus (1) must be negative for (4) to take place at all. However, this represents a general condition for the reduction of silver ion to silver and is not specific for photographic development. Many investigations have been made to determine whether the free energies of the processes exemplified by equations (2) and (3) indicate in a more specific way whether the reducing solutions in question are developers and what their photographic properties are. The present chapter discusses these and related investigations.

The free energies of systems which are thermodynamically reversible (see below) can be determined by measurements of electrochemical potentials, *i.e.*, of *redox potentials*, in the special case of oxidation-reduction processes. An example is the ferrous-ferric system (2). In other cases, the oxidized or reduced form undergoes further reactions, *e.g.*, in the hydroquinone-quinone system (3), where the quinone is unstable at a high pH. Here, allowance must be made for the ensuing deterioration of the system; for example, by extrapolation to zero time (see below). Then the potentials of these quasi-reversible systems are again a measure of the free energies of the redox processes proper.

The redox potential E is the potential between an inert electrode and the solution of a reducing or oxidizing compound in which the electrode is immersed. The reduced form of the compound offers electrons, while the oxidized form is ready to accept them. Thus, the electrode is exposed to a certain "pressure" of electrons, which depends on the relative concentrations of reduced and oxidized forms and on their chemical natures. It has been mentioned before that, for a thermodynamically reversible or quasi-reversible system, E is a measure of the free energy change, ΔF. E and ΔF are related by the equation $-\Delta F = Enf$, where n is the number of electrons involved in the reaction and f, one faraday. The redox potential for reversible or quasi-reversible systems is given in equation (5), which is derived from thermodynamic considerations of the free energy of reversible systems.

$$E = E_0 + \frac{RT}{nf} \ln \frac{(Ox)}{(Red)}. ^{*} \qquad (5)$$

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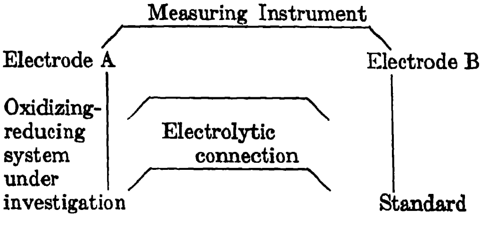
[*] According to this equation, a system with a higher potential oxidizes a system with a lower potential. The convention so established has been followed throughout this chapter because it is used in all the literature dealing with photographic developing agents and developers.

E_0 is the standard redox potential, a constant characteristic of the system; R is the gas constant; T, the absolute temperature; n and f were explained above. The numerical value for $\frac{RT}{f}$ at 20° C. is 0.0581 if decadic logarithms are introduced. The parentheses indicate the concentrations[*] of the oxidized and the reduced forms. If these concentrations are equal, *i.e.*, if the system contains 50 per cent of the oxidized and 50 per cent of the reduced state, the value of the second term of equation (5) becomes zero, and E is equal to the standard potential E_0, which is characteristic for the system. Equation (5) shows further that the more the system deviates from the 1 : 1 ratio, the more sensitive it becomes to changes in the concentration of the less concentrated compound. Potentials of reducing or oxidizing agents cannot be reproducible unless the alternate state is present in a definite concentration. A system the potential of which is not very sensitive to changes in the concentrations of the components is called *well poised*,[†] or said to have a good *buffering* capacity, while the very sensitive systems are called *unpoised.*

If Ox/Red is varied and E plotted against $\ln Ox/\text{Red}$, a straight line results, the slope (s) of which gives the value of $\frac{RT}{nf}$; hence, $n = \frac{0.0581}{s}$ at 20° C.

To measure the potential, a suitable chain is set up by combination with a standard. In appropriate combinations, the potential between A and B is the sum of the potentials A/liquid and B/liquid. As a standard reference electrode, the normal hydrogen electrode is usually chosen, while the actual measurement is made with a more convenient standard, *e.g.*, the calomel



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[*] Strictly, thermodynamic activities instead of concentrations should be used, but for the present purpose this correction may be disregarded.[1]

[†] This term was introduced by W. M. Clark.[2]

half-cell. Unless otherwise stated, the potentials given in this chapter refer to the normal hydrogen electrode. If the above-mentioned chain is allowed to do work, *i.e.*, to furnish a current, the reduced state goes over into the oxidized state, or vice versa. A system is thermodynamically reversible if, for infinitely small changes, the same amount of current, when it is passed through the chain in the opposite direction, reverses the chemical change quantitatively. Hence, all thermodynamically reversible systems are chemically reversible, but not all chemically reversible systems are thermodynamically reversible.

A very convenient method for varying Ox/Red in a system where the oxidized form of a substance cannot easily be determined has been worked out by Clark.[3] An oxidizing agent is added to a solution which contains the reduced form of a substance in a known concentration. This oxidizing agent is so chosen that in equilibrium it is almost completely reduced, so that the added amount of oxidizing agent is equivalent to the oxidized amount of the original substance; in this way, the concentrations of the oxidized and reduced form in the solution are known, and a determination of E gives the value for E_0.

As mentioned before, in the study of unstable solutions, care must be taken of the deterioration of the systems. A common cause for this deterioration in investigations of developing agents is the aerial oxidation of the reduced and, sometimes also, of the oxidized forms. To avoid this, the solutions should be kept in an atmosphere free from oxygen. However, other types of deterioration are independent of the presence of atmospheric oxygen; for example, disproportionations of the oxidized forms, condensations, and so forth. To avoid these changes, Clark, Cohen, and Gibbs[4] determined the potentials as quickly as possible and checked, by repetition of the measurements, that no considerable drift had occurred before the first observation was completed. Fieser[5] employed the method of discontinuous titration for the same purpose. To a solution of the reductant was added an amount of oxidizing agent estimated to produce a certain amount of the oxidant and, thus, to fix, at least momentarily, the ratio of oxidant to reductant. The potential of the solution was observed and followed in time, and the original potential was then found by extrapolation of the time-potential curve to zero time. In further experiments, the same quantity of reductant was treated with varying amounts of oxidizing agent, so that when all of the experiments were grouped together, a composite titration curve could be constructed, and from it the standard redox potential and other constants could be calculated.

Another method was devised by Hartridge and Roughton:[6] A solution of the reducing substance under investigation and a solution of the oxidizing agent flow through a mixing chamber and then through a tube which at certain intervals is provided with electrodes. If the mixing rate is high in comparison with the oxidation rate, the potentials along the tube change according to the rate at which the oxidation takes place. With a stable system, for instance, Fe^{+++}, Fe^{++}, the potentials measured along the tube approach certain constant values. However, with a deteriorating system, the change in potential due to the deterioration is superimposed on the change caused by the oxidation process. An analysis of the time-potential curve gives the rates of the two processes and accounts for the effect of the deterioration of the system on the potential.

Redox potentials have been measured not only on reversible systems but also on irreversible systems and on systems undergoing uncontrolled changes. These potentials cannot be considered to be measures of the free energies of the systems. However, experiments have shown that these potentials can be correlated with some of the photographic properties of the solutions and they are therefore of interest. It may be pointed out here that the correlation of electrochemical potentials to other, *e.g.*, photographic, properties of the systems is always permissible if the values are determined with due care in a reproducible manner. The establishment of these correlations may have some value for practical purposes, even if the data are not understood theoretically. On the other hand, data of obscure theoretical significance should not be interpreted by means of theories and formulas not applicable to them.

Early measurements of the redox potentials of a series of common reducing and oxidizing agents were made at W. Ostwald's suggestion by Bancroft.[7] However, these measurements were deficient in that the concentrations of the compounds in the opposite redox states remained undefined.

For such systems as ferrous-ferric ions, the expression for the electrode potential is given by the equation

$$E = E_0\text{Fe}^{+++},\ \text{Fe}^{++} + \frac{RT}{F}\ln\frac{\text{Fe}^{+++}}{\text{Fe}^{++}}. \qquad (7)$$

Theoretically pure ferric chloride should show a potential of $+\infty$; theoretically pure ferrous chloride, a potential of $-\infty$. All practically possible compounds contain, of course, at least traces of the opposite form, and the potentials have finite values.

TABLE XLV

Redox Potential in a Solution of 10 cm³ 0.25 mol $FeSO_4$ + 10 cm³ 0.25 mol $Fe(SO_4)_{1.5}$ with x cm³ 1.0 mol Na Salt of Organic Acid

a. *Citric acid*		b. *Malonic acid*		c. *Oxalic acid*		d. *Tartaric acid*		e. *Lactic acid*	
x	E	x	E	x	E	x	E	x	E
0	0.638	0	0.638	0	0.641	0	0.639	0	0.641
1	0.615	1	0.625	1	0.627	1	0.618	1	0.633
2	0.584	2	0.605	2	0.603	2	0.590	2	0.624
3	0.511	3	0.581	3	0.573	3	0.545	3	0.615
3.5	0.415	4	0.548	4	0.531	4	0.483	4	0.604
4.0	0.288	5	0.501	5	0.478	5	0.425	5	0.590
4.5	0.215	6	0.441	6	0.411	6	0.383	6	0.575
5.0	0.176	7	0.368	6.5	0.370	7	0.354	7	0.560
6	0.132	8	0.275	7.0	0.323	8	0.327	8	0.541
7	0.102	9	0.198	7.5	0.274	9	0.308	9	0.522
8	0.083	10	0.153	8.0	0.235	10	0.293	10	0.500
9	0.069	11	0.122	9.0	0.173			12	0.459
10	0.059	12	0.100					14	0.421
12	0.047	13	0.084					16	0.390
15	0.039	14	0.071	12.5	0.061			18	0.369
		15	0.065	14	0.045			20	0.348
		16	0.058	16	0.035				
				20	0.027				
				25	0.023				

When sodium fluoride is added to practically pure ferrous chloride, the potential is lowered by several hundred millivolts, because the Fe^{+++} present is largely eliminated through the formation of the complex FeF_6^{---} ion, while Fe^{++} does not, to an appreciable degree, form a similar complex. It was mentioned in Chapter IX, page 333, that a solution of ferrous salt which is not a photographic developer acquires developing properties upon the addition of fluoride ion.

A rather extensive research on the potentials of ferrous-ferric solutions containing organic complex-forming acids was made by Reinders and deMinjer:[8] Mixed solutions of ferrous sulfate and ferric sulfate were potentiometrically titrated with the alkali salts of citric acid, malonic acid, oxalic acid, tartaric acid, and lactic acid. The results are given in Table XLV. The potentials of the solutions varied between 0.641 and 0.023 volt, according to the concentration of the organic salt. The titration curves for the citrate and the malonate are given in Figure 125. Since the ferric complex is much less dissociated than the ferrous complex, upon addition of the organic salt the ferric complex will be formed first. Only when the ferric ions are used up will the organic ions form the ferrous complex. A marked fall in the potential curve, *i.e.*, the bend in this curve, indicates when all the ferric ions have been consumed; and from the curves, the existence of the complex ferric ions $Fe_2(C_6H_5O_7)_3^{---}$, $Fe(C_3H_2O_4)_3^{---}$, and $Fe(C_2O_4)_3^{---}$ can be deduced.

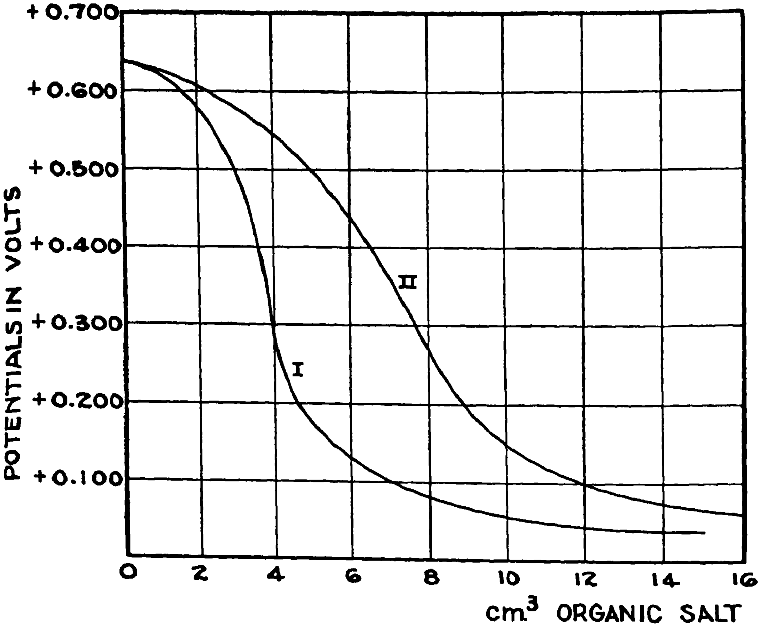


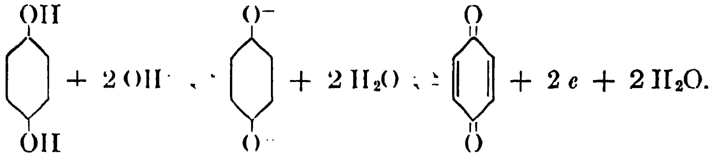
FIG. 125. Potentials of ferrous and ferric solutions with varying amounts of (I) citrate and (II) malonate.

Upon the addition of acid, the potential of the citrate- and malonate-containing solutions rises slowly, corresponding to the decrease in the concentration of the citrate and malonate ions. The addition of acid to the oxalate-containing solutions has less effect. On the addition of caustic soda, the potentials fall; but some solutions produce precipitates. However, a considerable amount of sodium hydroxide can be added to the solutions containing tartrate, and this lowers the potentials very markedly. The effect of the pH on the potentials is caused by the formation of complex ions which are different from those which are stable at lower pH.

In systems of the hydroquinone-quinone type, the potentials depend greatly on the pH of the solutions. They may be considered as determined by the concentrations of the oxidized form and of the divalent ion of the reduced form. The following equation then results:

$$E = E_0 + \frac{RT}{2f} \ln \frac{(C_6H_4O_2)}{(C_6H_4O_2{}^{--})} = E_0 + \frac{RT}{2f} \ln \frac{(\text{Quinone})}{(\text{Hydroquinone})^*} + \frac{RT}{2f} \ln \frac{K_1K_2 + K_1(H^+) + (H^+)^2}{K_1K_2}. \quad (8)$$

K_1 and K_2 are the first and second dissociation constants of hydroquinone. The importance attached to the divalent ion corresponds to the fact that neither the undissociated hydroquinone nor the monovalent ion can form quinone simply by losing electrons, while the divalent ion and quinone differ from each other only in their electrons:



(9)

This provides a convenient picture of the processes involved, but it should be remembered that the thermodynamic results are independent of the mechanism by which they are reached. This is treated in detail by Clark.[9] Each of the processes of equation (9), ionization and oxidation, can take place in two steps. This has been known for a long time for ionization, and it has been established for oxidation by Michaelis and his collaborators,[10] who demonstrated by analysis of the titration curves that electrons can be lost and added individually.

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* Analytical concentration, *i.e.*, concentration of molecules plus ions.

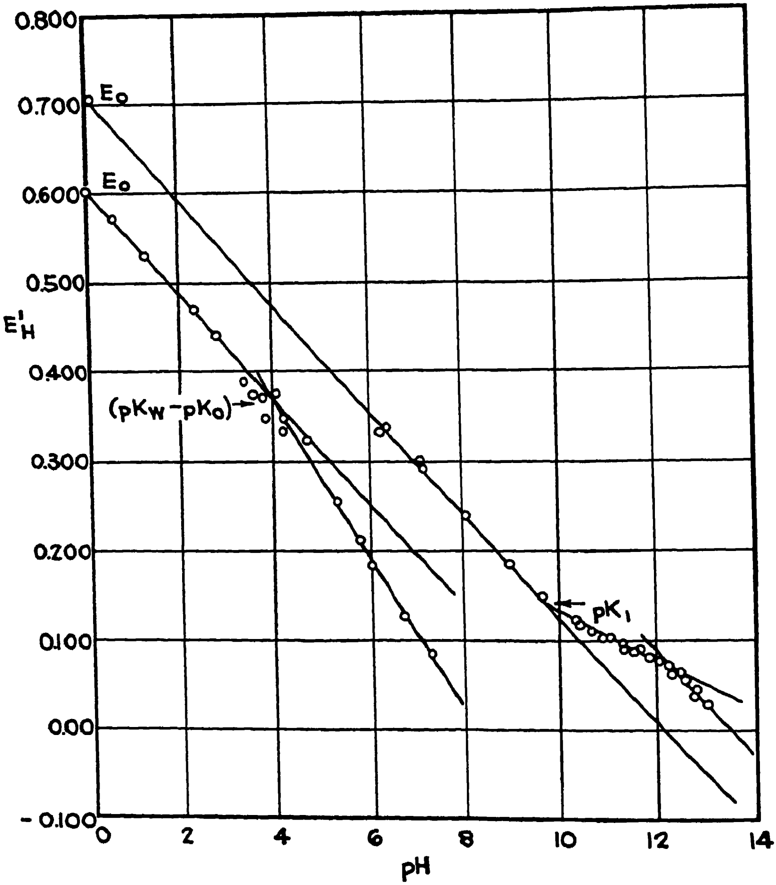


FIG. 126. The oxidation-reduction potentials (E'_H) of hydroquinone (upper curve) and of hydroxyhydroquinone (lower curve) in equilibrium with equal mols of their oxidation products at 20° C.

The normal potentials of the hydroquinone-quinone system (the values of the standard potentials E_0 at pH = 0, *i.e.*, in totally dissociated 1-normal acid) were studied by various authors,[11] and most recently Ball and Chen[6b] and Cameron[12] determined the standard potentials over a wide range of pH. Ball and Chen used Hartridge and Roughton's method (see page 474) and determined E_0 for a pH range of 0.9 to 12.5. Their values agree fairly well with the very complete determinations by Cameron. Cameron used the method of discontinuous titration described on page 473 and, working in an atmosphere of nitrogen to avoid autoxidation, obtained the results given in Figure 126. The following discussion is taken from his paper. The potential falls rapidly with increasing alkalinity of the solution. When (Red) = (*Ox*), the second member of equation (8) becomes zero, and the slope for the dependence of the redox potential upon pH should be 0.058 until the pK of the first ionization constant is reached, *i.e.*, the pH at which the concentration of the monovalent ion equals that of the undissociated hydroquinone or, roughly, the pH at which 50 per cent of the hydroquinone is ionized. Then the slope should become 0.029, and, at the pK of the second ionization, it should become zero.[1] Examination of Figure 126 shows that the change at the pK of the first ionization occurs, but that at about the point where the pK of the second ionization should be, the slope reverts to the original 0.058. Furthermore, the slope between pH 9.8 and pH 12.3 is not the theoretical 0.029 but 0.0261. This irregular slope indicates that in this region the potential is determined by a mixture of systems. At pH 12.3, the benzohydroquinone-quinone system must disappear as far as any effect upon the potentials is concerned; a change in slope at this point would indicate that a group common to both forms of the system had ionized in the oxidized form. Disappearance of the quinone in the range of pH above 10 is accompanied by the formation of a deep orange-red coloration which fades more or less rapidly, depending upon the pH value, to a yellow. The drift of potential is rapid.

It is known that at high pH a very rapid disproportionation of quinone into hydroquinone and hydroxyquinone occurs,

$$2\,C_6H_4O_2 + H_2O \rightarrow C_6H_4(OH)_2 + C_6H_3(OH)O_2,$$

which may be followed by the analogous formation of hydroxyhydroquinone and dihydroxyquinone,

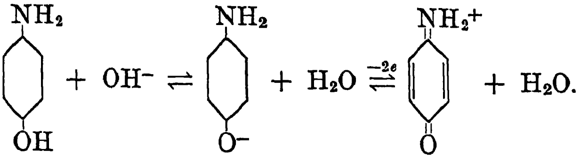
$$2\,C_6H_3(OH)O_2 + H_2O \rightarrow C_6H_3(OH)_3 + C_6H_2(OH)_2O_2.$$

Thus, at pH higher than 10, the mixtures in which the potentials were determined might contain hydroxyhydroquinone in equilibrium with dihydroxyquinone. The formation of the former system in the reaction mixtures was confirmed by experiments in which quinone solutions without hydroquinone were added to the buffers. The potentials and the color sequence of these solutions checked perfectly with those made up with hydroquinone and quinone. The fate of quinone in an alkaline solution was further illustrated by the following experiment: A measured quantity of acidified benzoquinone solution was reduced with hydrogen and colloidal palladium at pH 0.5 and titrated with potassium molybdicyanide solution in an inert atmosphere. The same quantity of quinone solution was then added to 0.1 M sodium hydroxide in an atmosphere of nitrogen, and after thirty minutes the solution was acidified with sulfuric acid to a pH of 0.5 and titrated with molybdicyanide solution. The titration indicated that 9.2 per cent of a compound 0.100 volt more negative in oxidation-reduction potential than the benzohydroquinone system and 67.7 per cent of hydroquinone had been formed from the quinone upon disproportionation in alkaline solution.

Ball and Chen also determined the redox potentials of catechol, protocatechuic acid, protocatechuic acid ester, gentisic acid, gentisic acid ester, pyrogallol, and pyrogallic acid—however, only in the pH range lower than 2, in which these substances do not develop the latent image.

Values for the normal potentials (standard potentials at pH = 0) of the hydroxybenzene compounds are given in Table XLVI. These compounds are developing agents with the exception of the acids 2, 5, and 9 (Chapter IX, p. 344).

The dependence of the redox potentials of *p*-aminophenols upon their pH is indicated by the equation


NH_2
OH
$+ OH^- \rightleftharpoons$
NH_2
O^-
$+ H_2O \overset{-2e}{\rightleftharpoons}$
NH_2^+
O
$+ H_2O.$

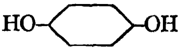
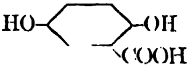
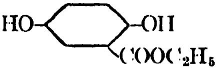
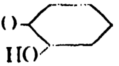
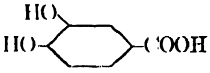
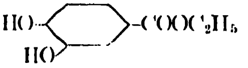
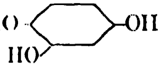
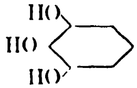
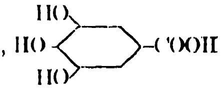
(10)

Here again, an anion (however, in this case, a monovalent one) is oxidized to a somewhat stable compound by the loss of two electrons. The un-ionized substance, to reach the same result, would have to lose an electron and a hydrogen atom.

Fieser,[5] using the method of discontinuous titration, studied the redox potentials formed in the oxidation of the developing agents *p*-benzylaminophenol, *p*-methylaminophenol, *p*-aminophenol, and *p*-phenylenediamine. His values for the standard potentials of *p*-benzylaminophenol and *p*-aminophenol are plotted against pH in Figure 127; those of methyl *p*-aminophenol, in Figure 128. The values of the *p*-aminophenol system for higher pH, which are included in Figure 127, were determined by Bogdanov[13] using Fieser's method.

TABLE XLVI

NORMAL POTENTIALS OF HYDROXYBENZENE COMPOUNDS, TEMPERATURE 30° C.

Reductant	E_0 *for pH = 0*
1. Benzohydroquinone, 	0.7029
2. Gentisic acid, 	0.793
3. Ethyl ester of gentisic acid, 	0.793
4. Catechol, 	0.792
5. Protocatechuic acid, 	0.883
6. Ethyl ester of protocatechuic acid, 	0.884
7. Hydroxyhydroquinone, 	0.6014
8. Pyrogallol, 	0.713
9. Gallic acid, 	0.799

Cameron[12] derived the following equation including the alkaline range, and, using the same method as for the hydroquinone system, verified it experimentally for methyl p-aminophenol:

$$E = E_0 + \frac{RT}{f} \ln \frac{(Ox)}{(\text{Red})} + \frac{RT}{f} \ln (\text{H}^+) + \frac{RT}{f} \ln \frac{K_a K_w + K_w(\text{H}^+) + K_R(\text{H}^+)^2}{K_w + K_0(\text{H}^+)}. \quad (11)$$

Red and Ox are the analytical concentrations of the reduced and the oxidized forms, K_w is the dissociation constant of water,

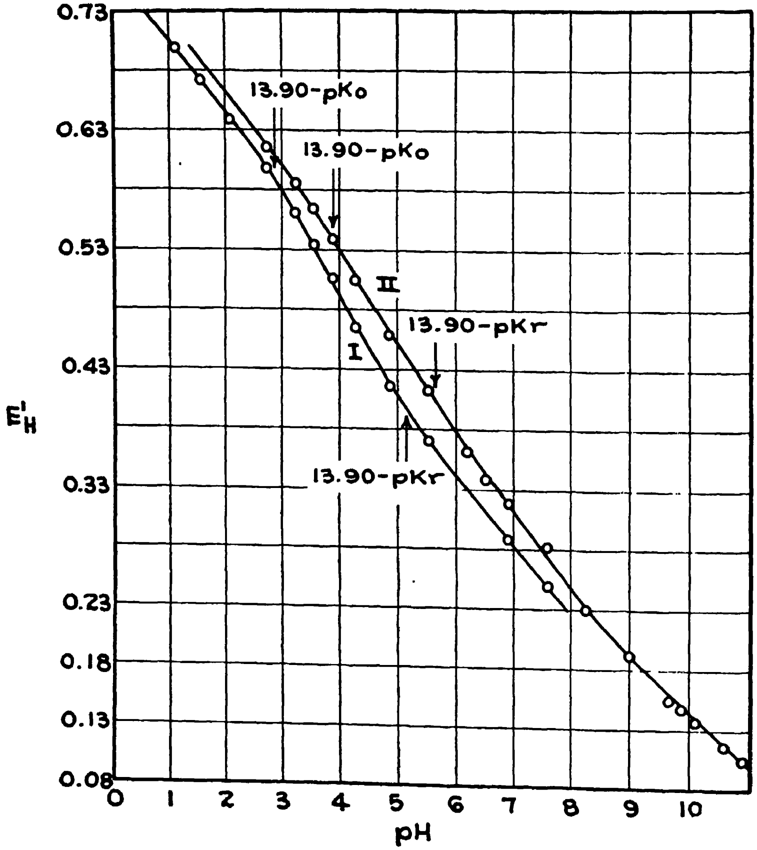


FIG. 127. Relationship between pH and the potential of half-oxidation (E'_H) of (I) p-benzylaminophenol and (II) p-aminophenol. (The lines are theoretical, the points experimental.)

K_a is the acid dissociation constant of the phenolic group in the reduced form, and K_0 and K_R are the basic ionization constants of the amino groups in the oxidized and the reduced forms. The normal potentials of the methyl *p*-aminophenol (metol) and the metol-sulfonic acid systems are plotted against the pH of the solutions in Figure 128. The lines are drawn with the theoretical slopes, and the curves show that the experimental data fit the calculated lines with excellent regularity. The introduction of the sulfonic acid group shifts all ionization constants so that both the acidic and the basic groups in metol are weakened and the redox potential at any given pH is increased. Cameron could carry the measurements into fairly alkaline solutions be-

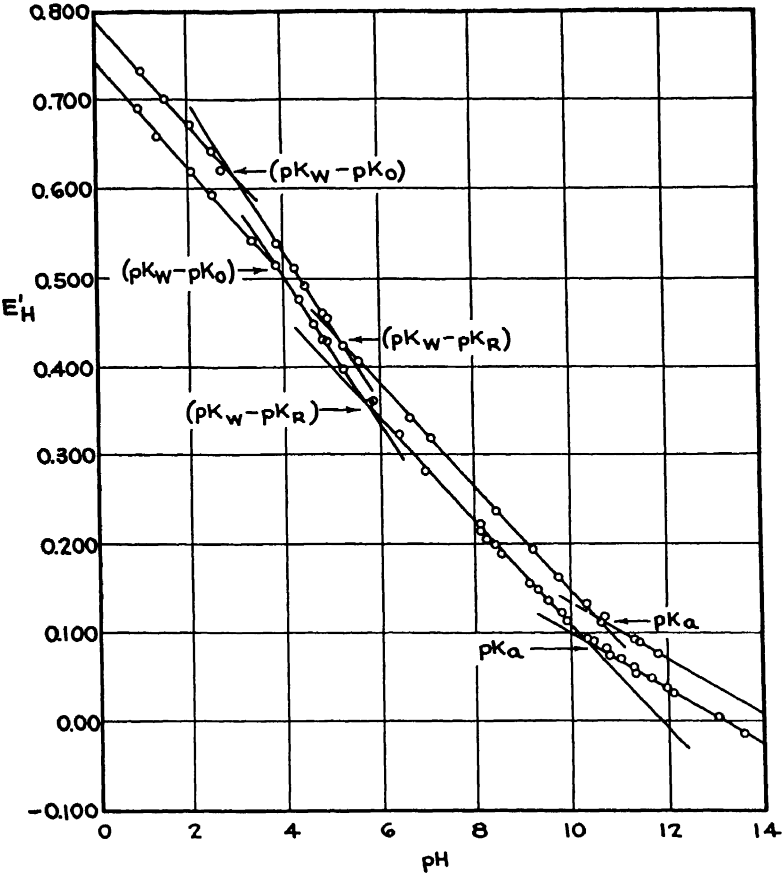


FIG. 128. The oxidation-reduction potentials (E'_H) of methyl-*p*-amino phenol (lower curve) and of methyl-*p*-aminophenol sulfonic acid (upper curve) in equilibrium with their oxidation products at 20° C.

fore the decomposition became too rapid. In all measurements of both compounds, the graph of the potential against time was a straight line for a considerable period. In some cases, it remained a straight line for fifteen minutes. The drift toward lower potentials indicated that the oxidized form was decreasing in concentration by a reaction the rate of which was unimolecular. No definite knowledge of the chemistry of this reaction is available at present.

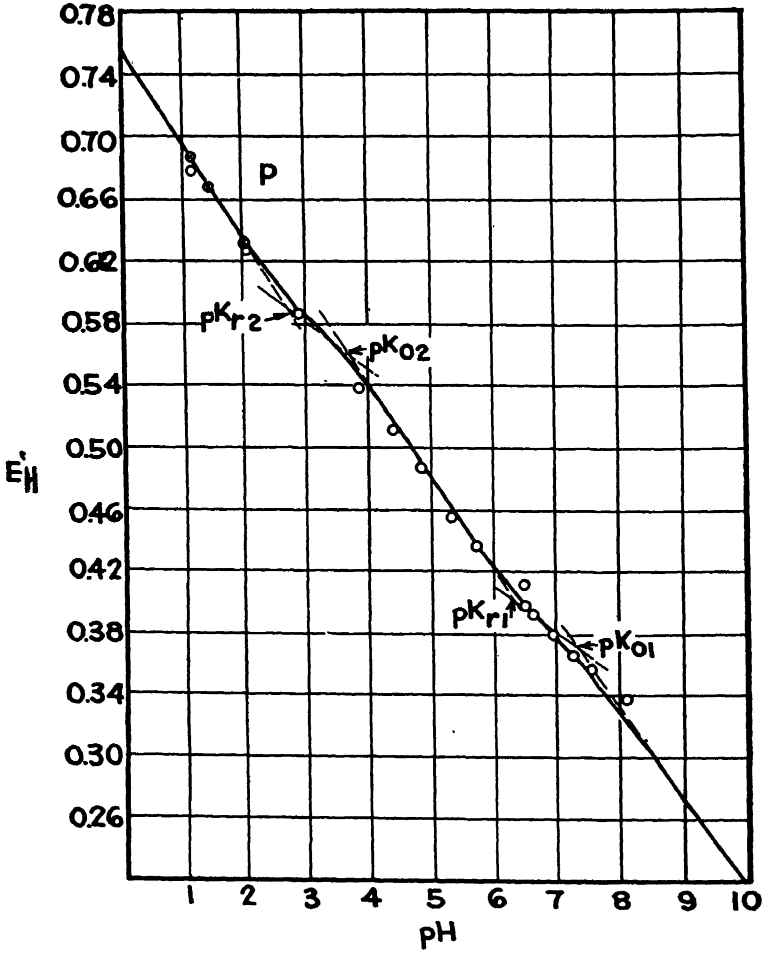
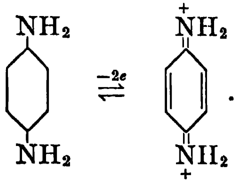


FIG. 129. The oxidation-reduction potentials (E'_H) of *p*-amino-*N*-dimethylaniline in equilibrium with its oxidation product at 20° C.

The dependence of the redox potentials on pH which is probable for *p*-phenylenediamine is indicated by the equation



(12)

The *p*-phenylenediamine system is so unstable in neutral solutions that Fieser could make measurements only at pH lower than 5. Clark, Cohen, and Gibbs[4] in an earlier attempt had not succeeded in measuring potentials of the *p*-phenylenediamine system. However, by rapid operation and using concentrated solutions in de-aerated buffers, they measured the potentials of the *p*-aminodimethylaniline system up to a pH of about 8. The results are given in Figure 129. Although the values conform perhaps as well to a "best straight line" as to the curve drawn in the figure, the latter is justified because it is in agreement with the independently determined dissociation constants involved, which are given in the figure as pK values. The subscript *r* indicates the reduced, *o* the oxidized form of the system.

TABLE XLVII

POTENTIALS OF NITROGEN-CONTAINING DEVELOPING AGENTS (ROUNDED AVERAGE VALUES, TEMPERATURE 25° C.)

System named as reductant	*Potential* *Alcohol* *v.*	*Potential* *Water* *v.*	*Half-life (neutral solution)* *Alcohol* *min.*	*Half-life (neutral solution)* *Water* *min.*
p-Methylaminophenol	0.693	0.688	35.6	7.4
p-Benzylaminophenol	.703	.698	3.9	1.4
p-Aminophenol	.733	.728	3.9	1.1
p-Phenylenediamine	.783	(.801)	0.5	0.1
N-Methyl-*p*-phenylenediamine	.751	..	0.5	..

Table XLVII, taken from Fieser, gives the potentials of some nitrogen-containing systems in aqueous and in alcoholic solutions. The potentials are those determined in dilute solutions of equimolecular quantities of the un-ionized oxidant and reductant and are referred to the hydrogen electrode in the same solvent. The half-life periods of the oxidized forms in these systems are also given to illustrate their instability.

To investigate the significance of redox potentials for photographic development, Bredig[14] used the potential values measured by Bancroft (p. 474) and potentials for silver bromide and silver chloride in potassium bromide solution which were calculated from measurements by Zengelis and Goodwin.[15] Bredig pointed out that the developer must have a lower redox potential than that of the silver halide, while systems with redox potentials as low as that of stannite fog the emulsion. He showed the connection between the restraining effect of acids on some developing agents and the decrease in the reduction potentials of the developing agents in acidic solutions. The effect of potassium bromide in developers was explained by the lowering of the oxidation potential of the silver halide.

The decrease of the standard reduction potentials with increasing pH is readily understood from the preceding discussion. It may be added that the increased developing activity of, for example, hydroquinone and *p*-aminophenol with higher pH may be connected with the lowering of the standard potentials and directly caused by the increased concentrations of the active ions. *p*-Phenylenediamine acts in a developer as the free base, and alkali must be added to neutralize the acid if compounds of this type are applied as salts. However, even after the pH of the solution has been raised enough for all the *p*-phenylenediamine to be present as the free base, a further increase in the pH of the solution has its effect on the rate of development. Superimposed on the electrochemical conditions are the kinetics of the various processes involved in photographic development. For instance, the removal of the quinonoid oxidation products is accelerated in alkaline media, and this may explain the dependence of the activity of *p*-phenylenediamine developers on the pH of the solution, even at alkalinities at which the compound is present only as the free base.[16]

It is mentioned in other chapters that, upon the addition of much bromide, a developer containing an oxidized form may even brominate a silver image already present, because the silver-ion concentration is lowered by the excess of bromide below the value which is in equilibrium with solid silver. The potential of a reversible silver/silver ion electrode is

$$E_{\mathrm{Ag}} = E_{0\,\mathrm{Ag}} + \frac{RT}{f} \ln \frac{(\mathrm{Ag}^+)}{(\mathrm{Ag})}, \qquad (13)$$

and obviously this potential will be affected by the presence of bromide ions. It was for this reason that Sheppard and Mees, Nietz, and others used the expression "bromide potential" for the decrease of development rate produced by bromide ions, since the Ostwald-Abegg theory of development implying a practically instantaneous establishment of the equilibrium between solution and solid considered the equilibrium conditions as decisive for the reaction rate. The method of determining bromide potentials was used not only because it reproduces the conditions of practical development fairly well, but because great difficulties were encountered in the measurement of the electrochemical redox potentials of most important developers. However, the true redox potentials cannot be calculated from the bromide potentials, and the quantitative study of the relation of true redox potentials to the properties of developers remained an interesting problem.

In the treatment of this problem, distinction should be made between investigations which use developers with well-balanced redox potentials, such as the ferrous-ferric systems containing complex-forming organic acids, and those using organic developing agents, such as hydroquinone and metol. It is obvious that the latter systems present all the difficulties encountered in the measurements of the redox potentials of the alkaline solutions of these developing agents. Furthermore, the difficulties are considerably increased by the fact that the developers do not contain reversible systems with reducing and oxidizing states in concentrations of the same order of magnitude. In the actual developers, the oxidants are present only in very small and unknown amounts. These systems are therefore badly poised and deficient in that the concentrations of the oxidized states remain undefined. If the developers contain sulfite, the small amounts of the oxidized compounds are further diminished by their reaction with the sulfite.

Frary and Nietz[17] attempted to measure the potentials of several common developers containing hydroquinone, metol and hydroquinone, amidol, and sulfite. Constant potentials were obtained only for certain solutions and after considerable time—one week to three months—the drift being attributed to the slow establishment of a certain concentration of hydrogen on the electrode. This was considered in agreement with a theory according to which the potentials of redox systems are caused by certain concentrations of hydrogen characteristic for the systems. Frary and Nietz calculated these concentrations from the measured potentials, but the physical significance of hydrogen pressures so determined is still undecided. The work demonstrated a variation of the potentials according to the circumstances of measurement, and Sheppard[18] in 1921 concluded that "at present, the measurements by electrical methods are entirely relative to the particular experimental conditions, and to a large extent, accidental."

It was shown above that Reinders and deMinjer succeeded in preparing ferrous-ferric systems which were well poised and graded according to their redox potentials. Reinders and Beukers used these solutions to study quantitatively the relationship between redox potentials of developers and some of their photographic qualities. Similar investigations were carried out independently by Faerman[19] and his colleagues.

According to equations (4), (5), and (13), one might expect development to proceed whenever $E_{Ag} > E$. However, Reinders and Beukers[20] found that to start development $E_{Ag} - E$ must attain a certain minimum value. The experiments, which resemble those of Sheppard and Mees described in Chapter IX, page 334, were carried out as follows: A series of solutions was prepared which contained ferrous and ferric ions in equal concentrations, potassium bromide in a molarity of 0.01, and varying amounts of the sodium citrate or sodium malonate. As shown in Table XLV, these reversible redox systems included potentials from 0.641 to 0.023 volt. A film was exposed so that, on full development, it would have had a density of about 3, and half of it was developed in a metol developer to a density of 0.82, while the other half was left unprocessed. The film was cut into nine strips, each strip comprising a developed and an undeveloped area. Each of eight of the strips was treated for twenty hours with one of the above-mentioned citrate-containing solutions, the ninth strip being treated with water only, as a control. The strips were fixed, washed, and dried. Figure 130 shows the results of these experiments. Curve I shows the densities of the predeveloped regions; curve II, those of the non-predeveloped regions, plotted against the redox potentials

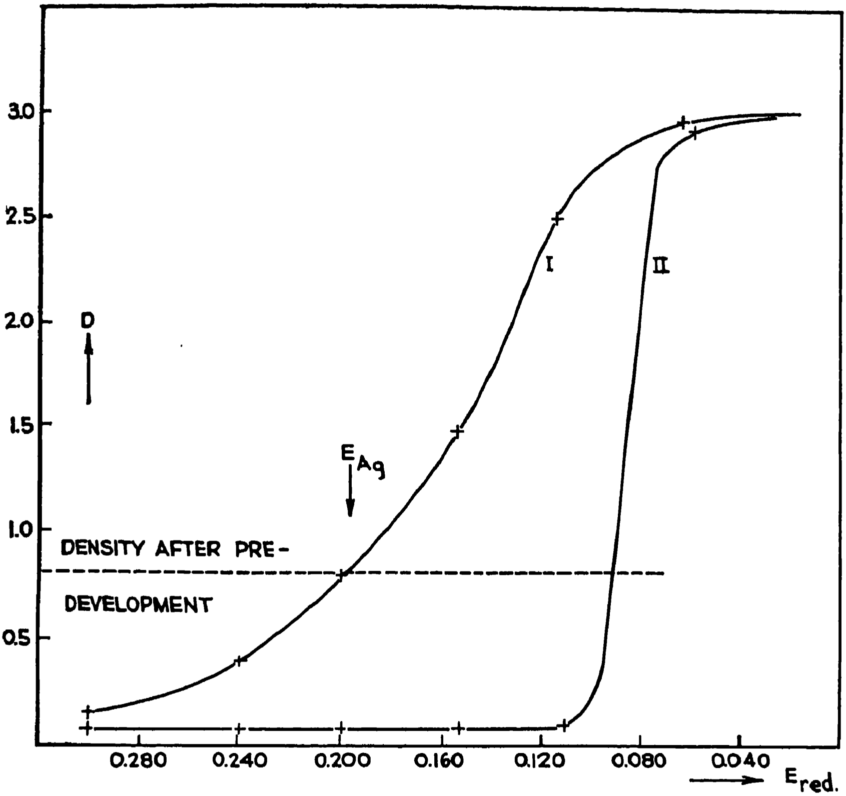


FIG. 130. Density of equally exposed strips after immersion in ferrous-ferric solutions with the indicated redox potentials: I, after exposure, predeveloped in metol-borax; II, as I, but not predeveloped.

of the solutions. Since the potential of a silver electrode in a 0.01 molar potassium bromide solution is 0.202 volts, it is evident from curve II that development does not start until ΔE, *i.e.*, $E_{Ag} - E$, has a value of about 80 mV. Developers with ΔE smaller than necessary for the initiation of development weaken the latent image, presumably because they dissolve the silver nuclei of the latter. Curve I, on the other hand, shows that development, once started, is continued if the value E of a solution is smaller than E_{Ag}, while rehalogenation occurs if E becomes greater than E_{Ag}.

Other experiments were carried out with varying exposures. In Figure 131, taken from Beukers' thesis, the fully drawn curves refer to experiments with predeveloped strips; the dotted lines, to experiments with non-predeveloped strips. Each curve of the two families represents a different exposure. The controls of the predeveloped strips are marked by small horizontal lines. To start development, the potential of the developer must be lower with smaller exposures, and the critical value ΔE varies between 70 and 100 mV. On the other hand, as might be expected, the exposure has no influence on the direction in which the developers affect the predeveloped image. Ferrous-ferric solutions containing malonate and other organic complex-formers produce the same values for the critical difference ΔE and for the equivalence potential, *i.e.*, the potential at which neither development nor rehalogenation occurs.

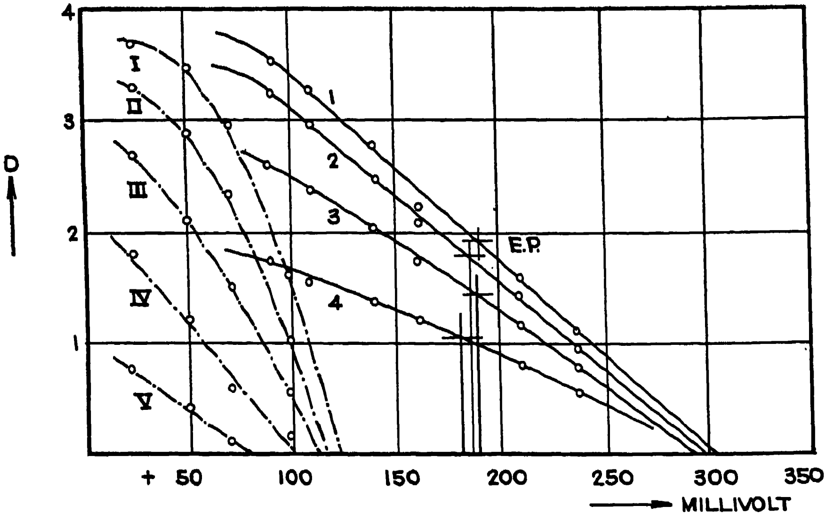


FIG. 131. Densities of strips with different exposures: Predeveloped strips 1, 2, 3, 4; log E, 3, 2.5, 2, 1.5; non-predeveloped strips I, II, III, IV, V; log E, 3, 2.5, 2, 1.5. Developer: Ferrous-ferric potassium malonate with potassium bromide.

Kameyama and Kikuchi[21] found that the critical values ΔE vary with the nature of the silver halides in a sequence which agrees with the solubility products. Table XLVIII shows the dependence of the silver potentials on the nature and concentration of the halides according to measurements by Reinders and Beukers.[22]

TABLE XLVIII

SILVER POTENTIAL OF SILVER HALIDES IN MILLIVOLTS, AT 18° C.

Silver chloride	in 0.001	N	potassium chloride	+397
Silver chloride	in 0.01	N	potassium chloride	+340
Silver chloride	in 0.1	N	potassium chloride	+286
Silver chloride	in 1.0	N	potassium chloride	+232
Silver bromide	in 0.001	N	potassium bromide	+254
Silver bromide	in 0.01	N	potassium bromide	+196
Silver bromide	in 0.1	N	potassium bromide	+138
Silver bromide	in 1.0	N	potassium bromide	+ 87
Silver iodide	in 0.001	N	potassium iodide	+ 35
Silver iodide	in 0.01	N	potassium iodide	− 23
Silver iodide	in 0.1	N	potassium iodide	− 81

For solutions containing equal amounts of hydroquinone and quinone, 0.005 mol per liter of potassium bromide, and no sulfite, the density of predeveloped strips increased when the pH was higher than about 8 and the redox potential lower than the silver potential, while solutions having a lower pH and a higher redox potential bleached the image. These experiments could not be extended into a more alkaline region because of the instability of the quinone at higher pH. According to Reinders and Beukers, the usual metol and metol-hydroquinone developers have redox potentials of about −25 to −50 mV., and they are not quite constant. The values for ΔE in this case would not be more than 200 mV. However, in view of the problems connected with the nature of organic developers (p. 487), it is difficult to say what importance can be attached to any of these statements.

For small differences between E_{Ag} and E, the rates of development and rehalogenation for the citrate-containing developer (Figure 130, curve I) are proportional to those differences. This holds also within certain limits for the other developers investigated. However, developers differ largely in their rates of development, even though they are adjusted to the same redox potentials. The malonate-containing solutions, for instance, are much more active than the citrate developers of the same potential. According to Bogdanov,[1] the ΔE values do not determine the speed of development. The lack of a relation between the development rates and the redox potentials of different developers was further demonstrated by Kan-Kagan.[23] The absence of such a relationship is not surprising, because the redox potentials depend upon the *ratio* of the concentrations of the oxidant to the reductant, while the rate of development should be primarily a function of the concentration of the active species of the developing agent itself, although this concentration is certainly not the only factor on which the rate of development depends.

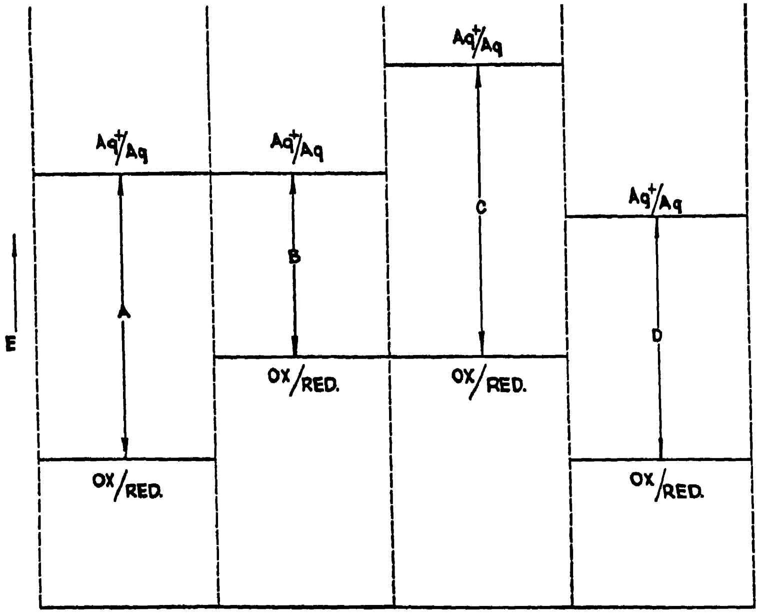


FIG. 132. Silver ion/silver and oxidation-reduction levels with different types of development.

A scheme to illustrate the significance of E_{Ag} and E for the different types of development was devised by Faerman [23b,18] and is shown in Figure 132. *A* represents the conditions for ordinary chemical development. In *B*, the redox potential of the developer is raised so that the value $E_{Ag} - E$ is insufficient for chemical development. In *C*, silver ions have been added to the developer and physical development proceeds. In *D*, the concentration of silver ions has been depressed by the addition of bromide, so that development slows down or even stops.

The necessity for a difference $E_{Ag} - E$ for the initiation of development is explained by Reinders, on the basis of the Ostwald-Abegg theory, by the small size of the silver particles which compose the latent image, while, for the continuation of development, larger aggregates of silver serve as centers of crystallization. It is known that the solubility of small particles is an inverse function of their size, and the concentration of a solution in contact with small particles increases with the solubility of these particles. Therefore, in equation (13), [Ag] increases and E_{Ag} decreases with the size of the silver particles, and a lower value of E is necessary to equal E_{Ag}, disturb the equilibrium, and start development. Reinders calculates that a concentration of silver atoms which is sixteen- to fifty-threefold greater than that of a solution in contact with macroscopic silver particles would account for a critical value of $E_{Ag} - E$ of 70 to 100 mV. The size of the particles producing this "supersaturation" was calculated by means of the Thompson-Ostwald equation, which shows the connection between the solubility and the dimensions of a particle. However, this equation does not hold if the particle size decreases to aggregates of a few atoms. The lower limit for the size of particles which will cause development is, therefore, according to Reinders and Hamburger,[24] too high when it is calculated by means of the Thompson-Ostwald equation with the observed values of ΔE. Reinders believes that an aggregate of four silver atoms is enough to initiate development, because this value was found in experiments in which silver was sublimed onto a glass plate and subjected to physical development. However, the calculations evaluating these experiments neglected the possibility of adlineation, mentioned on page 164, and may therefore have yielded particle sizes far too small.

Another aspect of the experiments of Reinders and Beukers concerns the magnitude of ΔE required to initiate reduction of the different grains of an emulsion. It is not quite clear whether in experiments in which development is carried to completion the densities still depend on the potentials of the developers as well as on the exposures. A dependence on the potentials would prove that the threshold value of E for the initiation of development varies from grain to grain. In terms of the Ostwald-Abegg-Reinders theory, this would mean that grains with larger silver nuclei become developable at E values at which grains with smaller nuclei are still unaffected by the developer. However, Socher[25] found that, in addition to the size of the silver particle, other factors, such as the adsorption of gelatin, may strongly influence the magnitude of ΔE. In general, the fact that a considerable difference between E_{Ag} and E is necessary for the initiation of development is in agreement not only with the development mechanism suggested by the Ostwald-Abegg theory but also with other mechanisms.

In physical development, the silver ions are added as a component to the developer, and the value $[Ag^+]$ on which the silver potentials depend is known to be regulated not only by the concentration of the soluble halide but also by the silver concentration of the developer and the nature and quantity of the complex-forming salts present.

Reinders and Beukers[22] determined the values of the silver potentials in solutions containing 0.1 mol of complex-forming salts and increasing quantities of silver nitrate (Table XLIX).

TABLE XLIX

SILVER POTENTIAL IN MILLIVOLTS IN SOLUTIONS CONTAINING PER LITER, 18° C.:

Millimol $AgNO_3$	*No Complex Forming Salt*	*0.1 g. mol* NH_3	*0.1 g. mol* Na_2SO_3	*0.1 g. mol* $Na_2S_2O_3$	*0.1 g. mol* KCN
0.2	+590	+280	+250	−68	−490
1.0	+630	+322	+294	−26	−467
2.0	+648	+340	+315	− 8	−455
4.0	+666	+358	+340	+ 8	−438
8.0	+683	+380	+372	+31	−417
12.0	+693	+397	+392	+47	−400
16.0	+700	+412	+411	+60	−386
20.0	+706	+422	+427	+73	−369

Potassium cyanide gives the strongest complex formation, followed by sodium thiosulfate and sodium sulfite. The addition of sodium sulfite to a solution of silver nitrate in sodium thiosulfate, therefore, does not change the potential. However, if thiosulfate is added to a complex solution of silver nitrate in sodium sulfite, the potential decreases very regularly with the thiosulfate content. The solution remains clear, and any desired silver potential between + 300 and + 30 mV. may thus be obtained. If still lower values are desired, they may be obtained by the addition of cyanide.

The values of the silver potentials explain the behavior of the respective solutions toward the silver halides. As shown in Table XLVIII, silver bromide in a 0.01 N potassium bromide solution has a potential of 196 mV. It therefore readily dissolves in a solution having a silver potential lower than + 196 mV.; *e.g.*, in the complex solution of sodium thiosulfate. However, in a 0.001 N potassium iodide solution, the silver potential is not higher than + 35 mV. Silver iodide therefore does not dissolve—or dissolves only slightly—in a physical developer which has a silver potential of +50 mV.; *e.g.*, in the physical developer of Odell (Table L, developer 6). According to Reinders and Beukers, this explains, at least partly, why, before treatment with the Odell developer, the film is bathed in a solution of potassium iodide. The grains of silver bromide are covered with a thin layer of silver iodide, and thus too rapid solution of the silver bromide in the developer is prevented. This would cause local overconcentration of the silver and possibly produce fog.

Reinders and Beukers determined the silver potentials and the reduction potentials for some practical physical developers containing organic reducing agents, in one case the reducer being left out of the solutions and in the other the silver nitrate; they measured the potentials with a silver electrode or a platinum electrode. The results are shown in Table L. If, in the table, the first strongly acidic solutions are neglected where the reduction potential of metol could not be determined with any exactness, it appears that, notwithstanding the widely varying compositions of these solutions, as well as the very different silver and reduction potentials, the value of ΔE will vary, within relatively close limits, from 100 to 170 mV. Reinders and Beukers point out that the spontaneous deposition of silver in solution 6, where ΔE is the smallest, was much less than in the other solutions. It was visible in solution 5 after three to four minutes; in solution 4, after one-half minute. The speed of the spontaneous silver formation thus increases with the value of ΔE.

The reduction potential in solution 6 was found to vary with the circumstances of the measurement. The value of − 50 mV. given in the table was observed after the solution was left standing for some time. If air was blown through it, the potential rose to 0 volts. Upon stopping the current of air, the potential decreased within five or ten minutes to − 50 mV. If the solution was then agitated, the potential increased again to a value between these limits, depending upon the intensity and the method of agitation. The other organic developers listed in Table L showed a similar behavior to a greater or less extent. The authors ascribe this phenomenon to the varying concentrations of the oxidation products of the developing agents, which depend on the rates of formation by aerial oxidation and on the rates of decomposition. If the solutions are stirred violently or air is blown through them, the concentrations of the oxidation products attain high values and the redox potentials are high. If the air stream or agitation is stopped, the dissolved oxygen is

TABLE L

THE FINAL SOLUTION CONTAINING IN GRAMS PER LITER:

No.	*Sodium Sulfite (anh.)*	*Sodium Thiosulfate (cryst.)*	*Other Materials*	*Reducer*	*Silver Nitrate*	e_{Ag} *mV.*	e_{Red} *mV.*	ΔE *mV.*
1	—	—	100 (citric acid) 15 (sodium citrate)	15–20 (metol)	3	710	+450	310
2	—	—	100 (citric acid)	20 (metol)	1	680	+450	280
3	40	25	20 (trisodium phosphate) (cryst.)	5 (amidol)	sat. silver bromide	+64	−95	159
4	153	—	—	3.3 (p-phenylenediamine)	6.25	270	+100	170
5	85	0.85	4 (ammonium thiocyanate)	16.5 (metol)	0.65	187	+50	137
6	20	32	—	1.67 (amidol)	3.2	+50	−50	100

1. Lüppo-Cramer, *vide* L. P. Clerc, *La technique photographique*, I, 375.
2. Lüppo-Cramer, *vide* E. v. Angerer, *Wissenschaftliche Photographie*, 20.
3. Lumière and Seyewetz, *vide* L. P. Clerc, *La technique photographique*, I, 373.
4. Lumière and Seyewetz, Eder's *Rezepte und Tabellen*, 1933, 86.
5. Neuhauss, *vide* L. David, *Photographisches Praktikum*, 1919, 389.
6. Odell, *The Camera* (Philadelphia), 1937, 54: 145.

used up. It is replenished only by oxygen entering by diffusion through the surface and the concentration in the lower layer and, therefore, the reduction potentials are low.

As mentioned on page 487, complications of this type might be anticipated in view of the experience with solutions of the organic developing agents themselves and the irreversibility and the lack of poise of the redox systems contained in developers. These complications are demonstrated in more detail by Cameron.[26] This author used for his measurements a water-jacketed beaker fitted with a glass cap carrying the necessary electrodes, salt bridge, stirrer, and so forth, so that any desired atmosphere could be maintained in this reaction vessel by introducing the gas through a bubble head. Rapid stirring with a motor-driven glass paddle which entered the reaction vessel through a water seal aided in securing equilibrium conditions. Solutions of metol and of hydroquinone were investigated in the presence of varying amounts of sulfite under nitrogen and in atmospheres which contained varying amounts of oxygen. Potentials measured in the absence of oxygen are much lower than those measured in its presence. In the absence of oxygen, the systems are unpoised, as would be expected of a solution containing only one component of a redox system. In the presence of oxygen, the potentials are lowered by sulfite in proportion to its concentration. This effect is in agreement with the assumption that the sulfite removes an oxidized form. The potentials of a metol solution containing sodium sulfite at pH 9 depend linearly upon the logarithms of the partial pressures of oxygen over the whole range from one to one hundred per cent of oxygen. Readings agreeing roughly with those obtained in pure nitrogen can be secured from electrodes located at the bottom of unstirred solutions exposed to air. As the oxygen present in the solution is used up, the potentials fall and become less well poised.

Cameron did not decide whether the oxygen functioned as a basic unit in the electrode reaction, setting up an oxygen electrode, or whether it acted on the potential by oxidizing the developing agent according to the mechanism suggested by Reinders and Beukers. Systems of the latter type were theoretically treated by Nekrasoff,[27] when he discussed the significance of the redox potentials of certain irreversible biological systems.

Nekrasoff shows that definite potentials may arise if there exists a definite "probability of appearance of hydrogen," *i.e.*, availability of electrons at the electrode. This will be the case if, for instance, a reducing compound is present in such an amount that its concentration does not vary perceptibly during the period of observation and if an oxidizing compound is formed and disposed of in such a way that a stationary state is set up and the concentration of the oxidant remains constant. For the potentials of irreversible systems with concentrations due to stationary states, Nekrasoff arrived at formulas identical with the usual formulas for redox potentials. However, the significance of these potentials is obviously different, because, inasmuch as they are not measured on reversible or quasi-reversible systems, they do not signify the free energies involved.

The potentials of these irreversible systems thus depend on the concentrations of substances which have only a fleeting existence. They are therefore susceptible to variations in the kinetics which determine the concentrations of the characteristic compounds, and, particularly, if the relative concentration of one compound of the system is low, a decided lack of poise and high sensitivity of the potentials may be expected.

To avoid the errors caused by the lack of poise and by the undetermined concentrations of the oxidants in the developers, the standard potentials of the developing agents rather than the potentials of the actual developers might be compared with the photographic results. However, the data available in the literature scarcely lead to the expectation that simple relationships might be found, even if the pH of the developers are the same as those for which the standard potentials were determined. Still less can a systematic relation be expected if the normal potentials (E_0 for pH = 0) of organic developing agents are compared with the photographic qualities of developers made up with these developing agents at entirely different pH values. Thus, Tables XLVI and XLVII show that compounds with identical normal potentials may or may not be developing agents, while compounds with rather different normal potentials may resemble each other in their photographic properties.

Another attempt to measure redox potentials in actual developers was made by Evans and Hanson:[28] The developer was placed in an open beaker and constantly stirred by a glass paddle. A small amount of potassium ferrocyanide was added as a potential mediator, because it was found that this increased the rate at which the electrodes came to equilibrium. From the reasoning on page 471, it is seen that this procedure should not appreciably affect the reduction potential of the system measured. The readings were commenced immediately upon insertion of the electrode. The potentials "customarily fell very rapidly at the start and then tapered off gradually to a well-defined equilibrium. This equilibrium was maintained for anywhere from thirty seconds to one-half hour, depending on the nature of the solution, and then drifted slowly to more negative values." Evans and Hanson state that this plateau was independent of the electrode material and was characteristic and repeatable for a given solution. It was taken as the true electrode potential of the solution under consideration. The numerical values given in the papers and used in the following discussion are the potentials actually measured against the saturated calomel electrode at room temperature and with the developer at 20° C. These values for typical mixed developers are presented in Table LI.

TABLE LI

REDUCTION POTENTIALS FOR TYPICAL MIXED DEVELOPERS

Formula[a]	*Type*	*pH*	*Reduction Potential volts*
D-1	Pyro	9.6	−0.364
D-9	Caustic hydroquinone	12.5	−0.446
D-16	Positive MQ	9.0	−0.295
D-72	Paper MQ	9.9	−0.407
D-76	Borax MQ	8.1	−0.259
D-76d	Buffered borax MQ	7.8	−0.253
D-82	High energy MQ	10.3	−0.420

[a] The formula designations refer to those published by the Eastman Kodak Company in its trade pamphlets. For the collected formulae, see *Elementary Photographic Chemistry*, published by the same company.

The dependence of the potentials on the concentration of the main constituents of the developer solutions, *i.e.*, the developing agent, the hydrogen ions, and the sulfite, was investigated. The change of the potentials to more negative values at higher pH, which is illustrated in Figure 133, may be due to an increased concentration of the negative ions of the developing agents and may also be caused by a shift in the concentrations of the oxida-

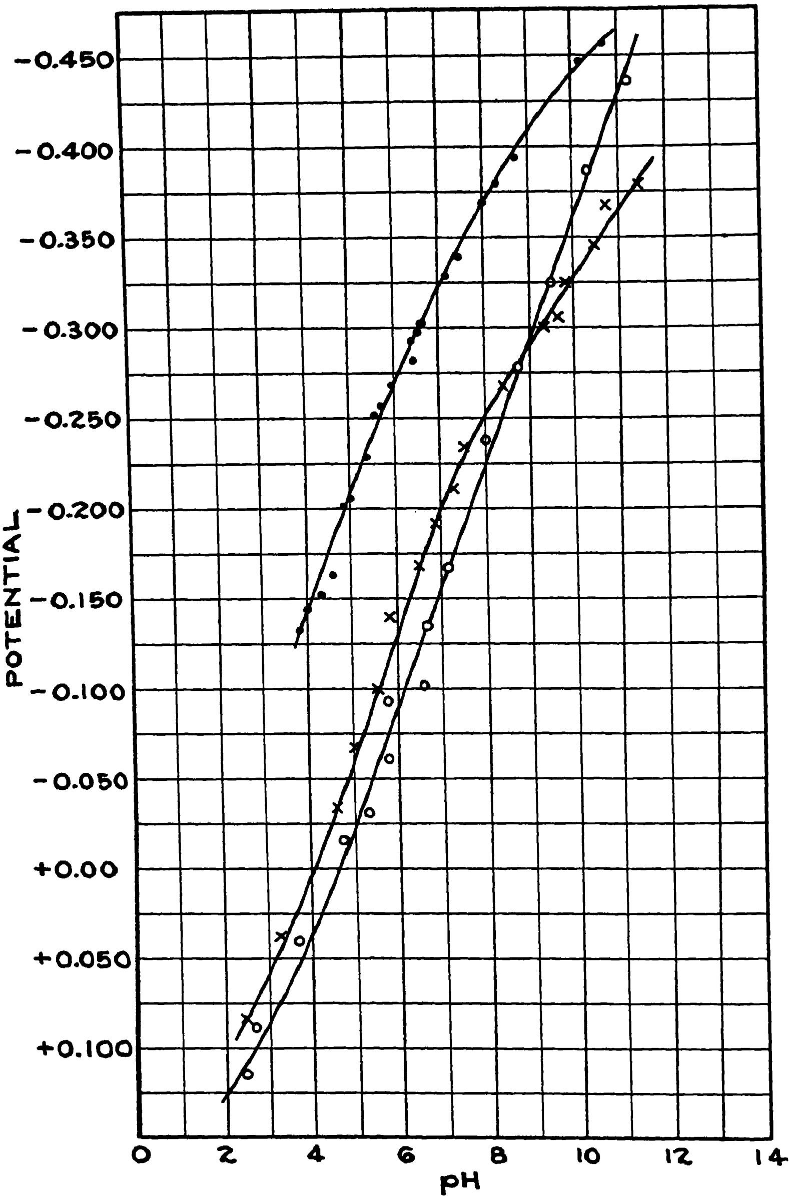


FIG. 133. Effect of pH changes on the potentials of developers: ●, amidol, 10 gms. per liter; sodium sulfite, 20 gms. per liter; ×, metol, 6.15 gms. per liter; sodium sulfite, 30 gms. per liter; o, hydroquinone, 5.5 gms. per liter; sodium sulfite, 30 gms. per liter.

tion products in more alkaline solutions. It should be noted that the sulfite concentration in the amidol developer is only two thirds of that in the other solutions. The effect of sulfite on the potential of an amidol solution is shown in Figure 134. The potentials fall as the sulfite concentration increases, not, however, in a linear proportion (p. 497); and the effect seems to approach a saturation value. The potential of an amidol solution of pH 7.9 containing sulfite proved to decrease linearly as the logarithm of the concentration of the developing agent rose.

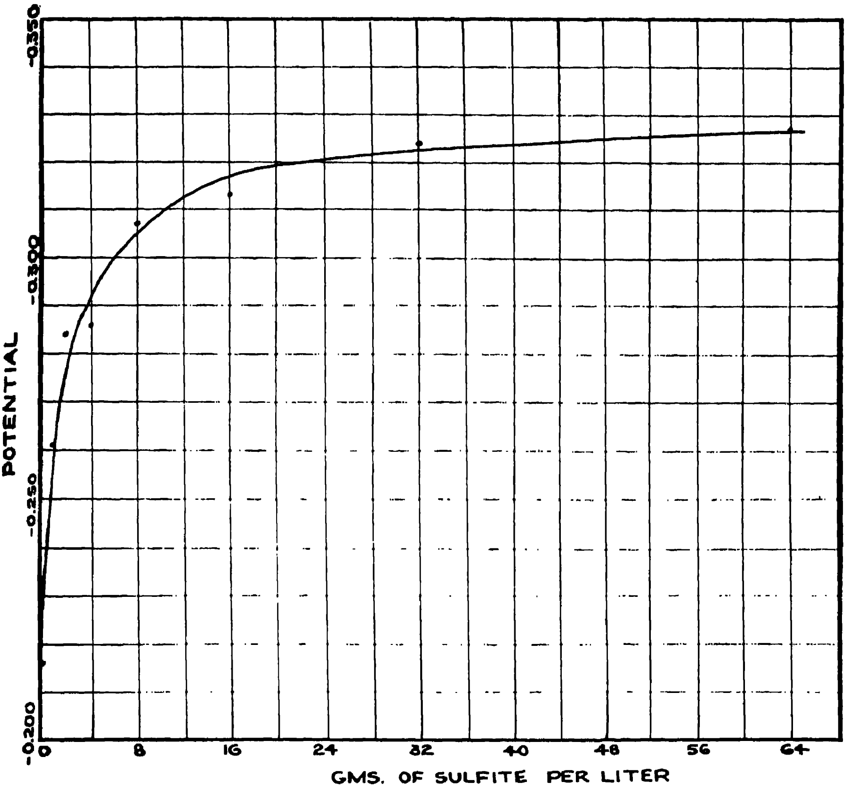


FIG. 134. Effect of sodium sulfite on the potential of an amidol solution. Amidol, 10 gms. per liter; pH = 6.1.

The above-mentioned potential measurements were used by Evans and Hanson in experiments which applied the methods of Sheppard and Mees and of Reinders and Beukers to organic developers. Most of this work was done with amidol, but according to the authors entirely analogous data were obtained with metol and hydroquinone. The potentials were varied for the most part by changing the pH of the solutions. However, the pH necessary for the solutions with high potentials would have been so low that the gelatin of the photographic material would have been attacked. In these cases, the reduction potential was raised by addition of an acidified solution of amidol which had been oxidized by air at a high pH. The developing experiments were carried out in large beakers "covered with heavy paper to exclude as much air as possible." The potentials of the solutions drifted somewhat during the course of development, and the potentials read immediately after development was completed, were therefore used in presenting the data. Development was continued for from five to six hours. Figure 135 shows the results for a developer containing 10 grams of amidol per liter and neither sulfite nor bromide. The full line curves give the values of the densities of the predeveloped strips corre-

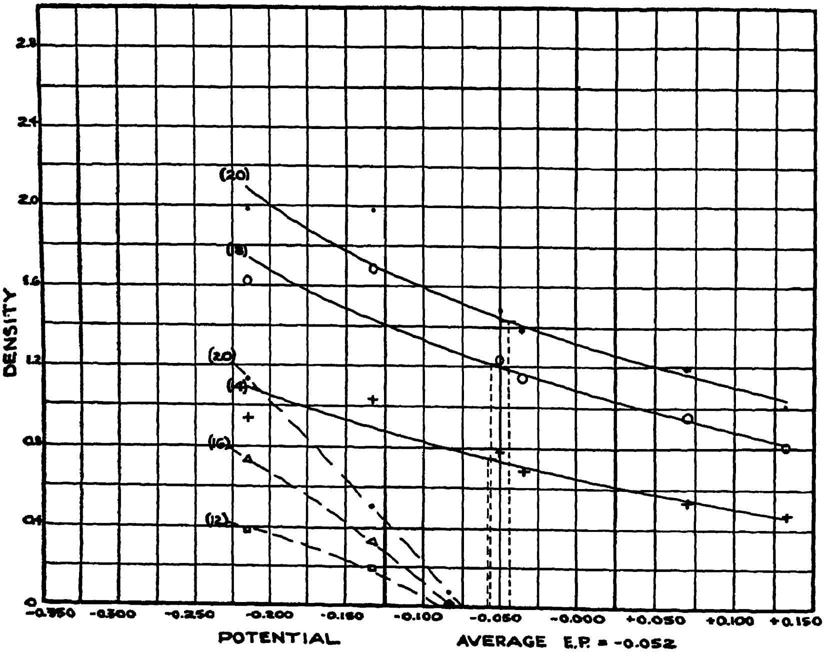


FIG. 135. Densities of strips with different exposures: (continuous line) predeveloped strips and (broken line) non-predeveloped strips.

sponding to the exposure step whose number is indicated in parentheses. The densities of the strips which had not been predeveloped are shown as broken lines. It is evident that in all essential respects the results of Evans and Hanson obtained with amidol correspond to those found by Reinders and Beukers

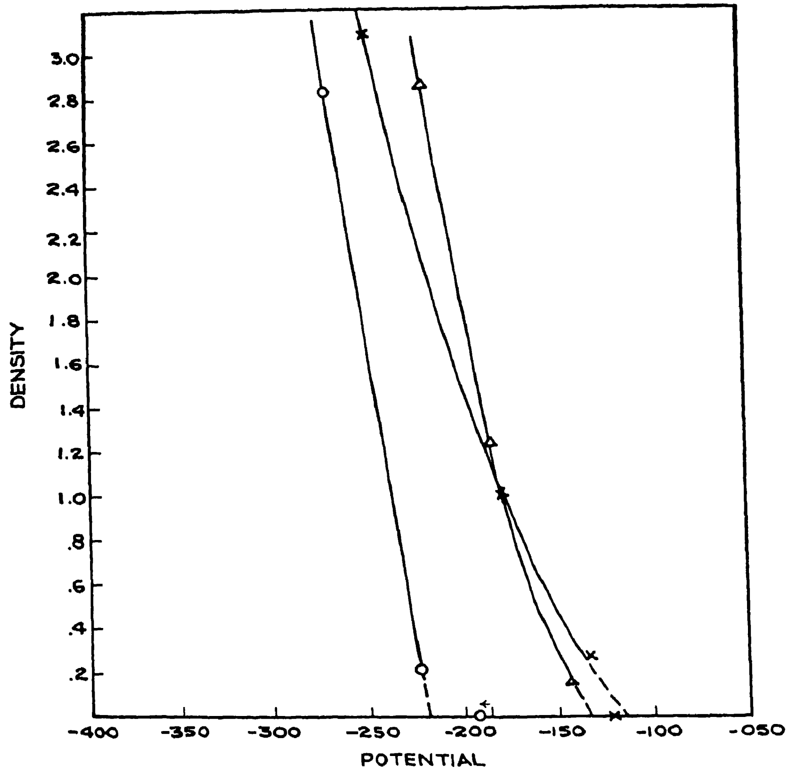


Fig. 136. Effect of the potential of the developer on the density produced: ×, amidoldihydrochloride, 6 hours; ○, hydroquinone, 22 hours; △, methyl-*p*-aminophenol sulfate, 6 hours. Developing agent, 10 gms. per liter; potassium bromide, 2 gms. per liter; sodium sulfite, 6.25 gms. per liter. Exposure, 0.5 m.c.s.

for development with ferrous complexes (see Figure 131), and, if correction is made for the reference electrode, even the values for the equivalence potentials agree within 10 mV. In a series with a developer containing sulfite, the same type of family of curves was obtained; and the equivalence potential was again the same.

To test the effect of bromide on the position of the equivalence potential and on the threshold potentials for the initiation of development, two series of experiments were run: A fourfold increase of the bromide concentration lowered both potentials by about 40 mV., in good agreement with the theory, since an evaluation of equation (13) produces a shift of 36 mV. Other experiments showed that the concentration of the amidol has a marked effect on the threshold potentials for the development of the latent image. As the concentration of the developing agent decreases, a lower potential is required to initiate development.

Potentials of developers with amidol, hydroquinone, and metol, plotted against the densities obtained for a given exposure, are shown in Figure 136. The difference between hydroquinone and metol or amidol is even more striking in view of the fact that the time of development with hydroquinone was nearly four times as great as that of either of the other developers, and its molar concentration was 50 per cent or more greater than theirs.

TABLE LII

ELECTROCHEMICAL REDUCTION POTENTIALS ACCORDING TO EVANS AND HANSON AND PHOTOGRAPHIC REDUCTION POTENTIALS ACCORDING TO NIETZ

		Reduction Potential		*Bromide Potential*	
Concentration	*Developing Agent*	*Cont. Nitrogen*	*Without Nitrogen*	*Cont. Nitrogen*	*Without Nitrogen*
M/20	Diaminophenol (amidol)	0.434		30–40	
M/25	Bromhydroquinone		0.327		21.0
M/20	Monomethyl *p*-aminophenol sulfate (metol)	0.308		20.0	
M/20	Pyrogallol		0.388		16.0
M/20	Dimethyl *p*-aminophenol sulfate	0.293		10.0	
M/20	Chlorhydroquinone		0.335		7.0
M/20	*p*-Aminophenol hydrochloride	0.291		6.0	
M/20	Toluhydroquinone		0.390		2.2
M/20	Hydroquinone		0.357		1.0

Evans and Hanson, furthermore, measured the redox potentials of solutions mixed to be as similar as possible to some developers for which Nietz had determined the photographic bromide potentials, π_{Br} (Chapter IX, page 352). Table LII allows a comparison to be made of the two types of potentials. The values are arranged so that the data for the developing agents with amino groups are separated from those for the developing agents without nitrogen. There is some parallelism between the two series of values in the former class. However, no apparent relationship exists with respect to the latter group of developers. The results of Evans and Hanson are of interest because they show the relation of the photographic data to the potentials measured by their method. However, it should be kept in mind that these potentials appear not to be true redox potentials of reversible systems, as shown by the investigations of other authors, and particularly of Cameron, as reported on page 479.

In another paper, Cameron[20] showed that, with a sulfite-containing metol developer, no pH value could be found at which the predeveloped image was bleached and that the potential at which no change of density occurred, in comparison with the test strips, were not in agreement with the value of −0.150 volts given by Evans and Hanson for amidol at the same bromide concentration. The potential below which development was continued was not markedly influenced by a tenfold increase in the concentration of sulfite, while a fivefold increase in the metol concentration caused a shift to a lower pH value. The absence of a bleaching action in metol solutions containing sulfite confirms the fact that no reversible redox system exists in such solutions. A considerable variation appeared in the potentials of the same solution before and after development. The potential behavior of a platinum electrode after the film had been immersed in the solution for fifteen and a half hours proved to be very similar to that of a silver electrode.

In conclusion, it may be emphasized that in a practical developer which is badly poised the concentration of the oxidant depends not only on the chemical nature of the developing agent, on the pH of the solution, and on the concentration of sulfite, but also on the amount of silver reduced per unit of time. The concentrations of the oxidant and the reductant inside the emulsion may further be influenced by the diffusion rates of the various compounds, and this increases the difficulty of gauging the significance of experiments with organic developers.

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CHAPTER XIII

FIXATION AND WASHING

The processes following development may be divided into primary treatments, necessary to finish the picture or give some desired effect, and secondary ones, such as hardening, which are useful under certain conditions.

The most essential processes are fixing, washing, and drying. Hardening is necessary, in addition, in hot climates or under difficult commercial conditions. The fixing and hardening baths may be combined in a single formula, though they tend to involve incompatible materials. The operations may be classified as follows:

Primary After-treatment

A. Essential
    Fixing
    Washing
    Drying
B. Optional
    Intensification and reduction
    Toning
    Tinting

Secondary After-treatment

The acid stop bath
Hardening

THE CHEMISTRY OF FIXATION

Besides the reduced metal forming the image, the developed photograph contains the residual silver halide unaffected by the developer. It is held in a gelatin layer, which is swollen with a solution of sodium carbonate or other alkali and contains also partially oxidized products from the developer. Fixing should exert the primary function of dissolving the halide and the secondary one of stopping development, preventing organic stain, and hardening or checking the further swelling of the gelatin.

The character of the silver salt remaining undeveloped varies with the emulsion. Negative coatings generally contain silver bromide and some silver iodide; bromide papers, nearly pure silver bromide; while the emulsion of slow development papers is essentially pure silver chloride. Since the silver halides are only very slightly soluble, they cannot be removed from the emulsion by simple washing but must be treated with a "fixing" solution which can react with them to form soluble complex salts. From the mass action law,

$$\text{Ag X (solid)} \rightleftharpoons \text{Ag X (dissolved)} \rightleftharpoons \overset{+}{\text{Ag}} + \overset{-}{\text{X}},$$

assuming that the small quantity of dissolved silver halide is completely ionized,

$$[\text{Ag X}] = K[\overset{+}{\text{Ag}}][\overset{-}{\text{X}}];$$

or, since the active mass of the solid phase is a constant,

$$[\overset{+}{\text{Ag}}][\overset{-}{\text{X}}] = \text{constant} = \text{solubility product.}$$

Obviously, the solubility of the silver halide can be increased by reducing the active concentration of either or both of the ions. This is done by the formation of complex ions. If the complex ion has a very low dissociation factor, the silver ions will be removed from the field of action as rapidly as they are formed, with the result that the solubility of the silver halide is greatly increased.

The ultimate or basic criterion for the efficiency of a fixing bath is its stability, the reciprocal of the dissociation of the silver complex ion formed. Thus, if the complex ion dissociates according to the equation

$$\text{Ag}\,\overset{-}{\text{M}} \rightleftharpoons \overset{+}{\text{Ag}} + \overset{--}{\text{M}},$$

then,

$$\frac{[\overset{+}{\text{Ag}}][\overset{--}{\text{M}}]}{[\text{Ag}\,\overset{-}{\text{M}}]} = K',$$

where K' is the ionization constant. Its reciprocal value gives the *stability constant* of the fixing bath, K'':

$$\frac{1}{K'} = \frac{[\text{Ag}\,\overset{-}{\text{M}}]}{[\overset{+}{\text{Ag}}][\overset{--}{\text{M}}]} = K''.$$

The higher the value of K'', i.e., the lower the ionization constant, the higher the total silver concentration required to produce a given silver-ion concentration and the more soluble the silver halide. If several complexes are formed by the fixing agent, the stability of the least dissociated complex will determine the stability of the fixing bath. To insure complete solution of different silver salts, the stability constant of the fixing agent must be higher as the solubility product of the salt is lower. Thus, potassium or sodium cyanide is required to dissolve silver sulfide, the least soluble of silver compounds, and it is seen from the following table, quoted from Bodländer,[1] that the complex silver-cyanide ion is the most stable.

TABLE LIII

STABILITY CONSTANTS FOR SILVER COMPLEXES

Formula of Complex Ion	*Condition Electrically*	*Concentration Limit of Free Anion*	K''
$Ag(S_2O_3)_2^{---}$	Anion	Below 0.1 N	0.98×10^{13}
$Ag(S_2O_3)_3^{-----}$	Anion	Above 0.5 N	3.45×10^{13}
$Ag(CN)_2^{-}$	Anion	Under 0.05 N	0.11×10^{22}
$Ag_2I_4^{--}$ to AgI_4^{---}	Anion	Indefinite	7.7×10^{13}
$Ag(CNS)_2^{-}$	Anion	Below 0.2 N	6×10^{9}
$Ag(CNS)_3^{--}$	Anion	Above 0.3 N	1.5×10^{9}
$Ag(NH_3)_2^{+}$	Cation		0.15×10^{8}

A considerable number of materials form complexes with silver ions, some of which have stability constants sufficiently high to allow them to function as fixing agents for photographic emulsions. However, in addition to dissolving the silver halide, the fixing agent must form complexes which are stable upon dilution so that they will not decompose during washing. Also, the fixing agent should not attack the gelatin of the emulsion or affect the silver grains of the developed image.

Among the many silver solvents may be mentioned the sodium, potassium, and ammonium thiosulfates and thiocyanates, sodium and potassium cyanides, sodium sulfite, ammonia, thiourea, thiosinamine, and concentrated potassium iodide. Of these, however, all but the thiosulfates and cyanides are impractical either because of their high cost or from failure to meet one of the requirements mentioned above. The cyanides are objectionable because they are extremely poisonous, and in practice thiosulfates, particularly sodium thiosulfate or "hypo," are used almost exclusively as fixing agents.

The reactions between sodium thiosulfate and the silver halides are given generally in the photographic literature and textbooks as the following equations:

$$2\,AgX + Na_2S_2O_3 \rightarrow Ag_2S_2O_3 + 2\,NaX, \qquad (1)$$

$$Ag_2S_2O_3 + Na_2S_2O_3 \rightarrow Ag_2S_2O_3 \cdot Na_2S_2O_3, \qquad (2)$$

$$Ag_2S_2O_3 \cdot Na_2S_2O_3 + Na_2S_2O_3 \rightarrow Ag_2S_2O_3 \cdot 2\,Na_2S_2O_3. \qquad (3)$$

These are based upon analyses of compounds first isolated by Herschel.[2] However, as Baines[3] points out, the presence of silver cations in any appreciable amount would result in the formation of silver sulfide, since its solubility product is extremely low and a sufficient concentration of sulfide ions is produced by a slight decomposition of the thiosulfate. The existence of double salts is very unlikely, therefore, and the products of equations (2) and (3) could be present only as complex salts, with the silver as part of the complex ion. Instead of equation (1), Baines proposes

$$AgX + Na_2S_2O_3 \rightarrow NaX + NaAgS_2O_3. \qquad (1a)$$

The formation of complex ions was investigated, by means of e.m.f. measurements, by Bodländer,[4] who deduced the following formulas:

$$Ag(S_2O_3)^{-}, \qquad Ag(S_2O_3)_2^{---}, \qquad Ag(S_2O_3)_3^{-----}.$$

Sheppard[5] gave the ionic equations for the formation of these complexes:

$$\overset{+}{Ag} + S_2O_3 \rightarrow AgS_2O_3, \qquad (4)$$

$$AgS_2O_3 + S_2O_3 \rightarrow Ag(S_2O_3)_2^{---}, \qquad (5)$$

$$Ag(S_2O_3)_2 + S_2O_3 \rightarrow Ag(S_2O_3)_3^{-----}. \qquad (6)$$

Baines emphasized that silver cations would immediately disappear through the formation of these complexes in excess thiosulfate. Equation (4) corresponds, therefore, to equation (1a) and not to (1). Equation (2) can be regarded as identical with equation (1a) by producing 2 $NaAgS_2O_3$. None of the ionic equations corresponds to equation (3).

Many investigators have attempted to isolate the various double salts of sodium silver thiosulfate or, as they may more properly be called, the sodium salts of the argentothiosulfuric acids. The results indicate the existence of a considerable number of these compounds, and in Table LIV are listed those for the existence of which there is apparently reliable evidence. Probably all of these occur as hydrates, but owing to uncertainty as to the number of molecules of water combined with each form, only the formulas for the anhydrous salts are listed.

TABLE LIV

		Argentothiosulfate ion	*Reference*
$Ag_2S_2O_3$	Insoluble	—	(6)
$NaAgS_2O_3$	Slightly soluble	$AgS_2O_3^-$	(7)
$Na_6Ag_4(S_2O_3)_5$	—	$Ag_4(S_2O_3)_5^{------}$	(8)
$Na_5Ag_3(S_2O_3)_4$	Easily soluble	$Ag_3(S_2O_3)_4^{-----}$	(3)
$Na_4Ag_2(S_2O_3)_3$	Easily soluble	$Ag_2(S_2O_3)_3^{----}$	(9)
$Na_3Ag(S_2O_3)_2$	—	$Ag(S_2O_3)_2^{---}$	(4)
$Na_2S_2O_3$	—	—	

It is doubtful whether all of the ions mentioned actually exist in solution. As stated above, Bodländer[4] deduced the presence of the $AgS_2O_3^-$ and $Ag(S_2O_3)_2^{---}$ ions as well as the $Ag(S_2O_3)_3^{-----}$ ion, of which no solid salt has been isolated. Hunger[10] deduced the presence of $Ag_2(S_2O_3)_3^{----}$ in thiosulfate solutions saturated with AgCl, and both $Ag_2(S_2O_3)_3^{----}$ and $Ag(S_2O_3)_2^{---}$ in similar solutions saturated with AgBr, but only $Ag(S_2O_3)_2^{---}$ in solutions with AgI. Baines[3b] isolated monoargentomonothiosulfuric acid, $HAgS_2O_3$, in the crystalline form. He did not isolate the acid $H_5Ag_3(S_2O_3)_4$, but he advanced strong arguments for the existence of the ion $Ag_3(S_2O_3)_4^{-----}$ in solution and concluded from other experiments that the acid is stable in dilute solution but unstable in concentrated solution.

Other important investigations on the sodium silver thiosulfate complexes have been made by Spacu and Murgulescu,[11] Brintzinger and Eckardt,[12] and Bassett and Lemon.[13] The last named have investigated the system $Ag_2S_2O_3—Na_2S_2O_3—H_2O$ at 25° C., and express the results in the form of a phase rule diagram (Figure 137). They are of the opinion that only the following salts exist in contact with solutions of suitable composition: (1) $Na_3Ag(S_2O_3)_2 \cdot 2H_2O$, readily soluble in water; (2) $Na_5Ag_3(S_2O_3)_4 \cdot 2H_2O$, readily soluble; (3) $NaAgS_2O_3 \cdot H_2O$,

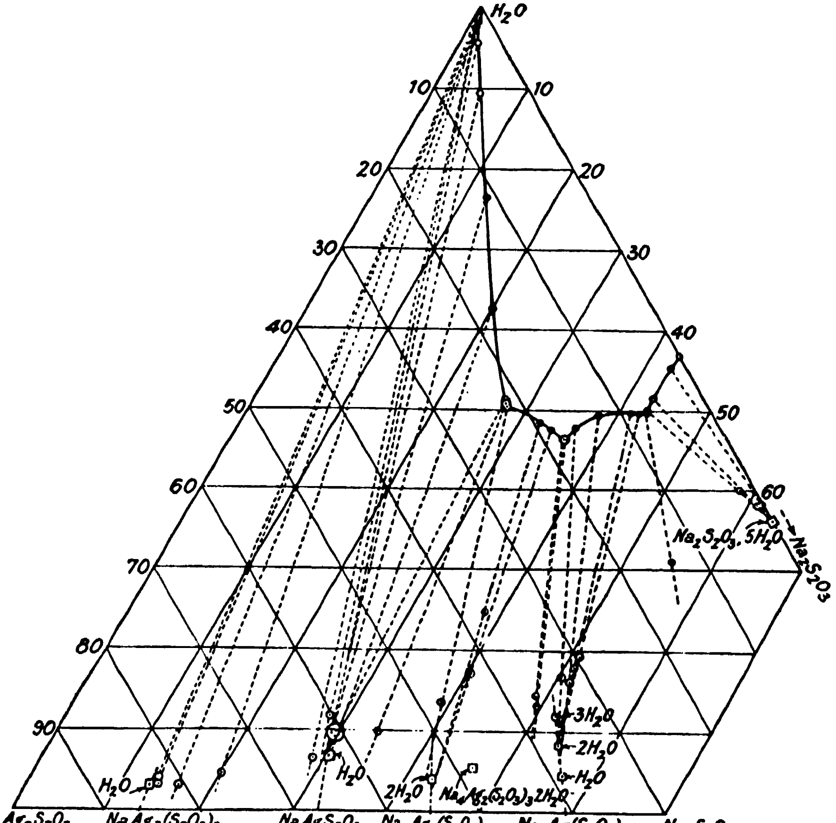

FIG. 137. Phase-rule diagram of the silver thiosulfate-sodium thiosulfate-water system.

sparingly soluble; and (4) $NaAg_3(S_2O_3)_2 H_2O$, very slightly soluble. They give evidence also which indicates that no salt richer in silver than $NaAg_3(S_2O_3)_2$ is present in thiosulfate solutions.

It seems probable that a mixture of the various ions in equilibrium with one another exists in any given solution and that the composition of the solid compound precipitated from the solution is dependent upon the condition and means of precipitation. In view of the great excess of thiosulfate, it is probable that practically all of the dissolved silver in a fixing bath exists as highly thiosulfated complexes.

The published data on the solubility of the silver halides in thiosulfate solutions, again, show considerable variations. This is not surprising in view of the demonstrated dependence of the solubility on particle size and other factors difficult to control. A redetermination of these solubilities is very desirable. The values given in Table LV are those obtained by Valenta [14] and Busch.[15]

TABLE LV

Concentration (Grams per Liter of Water)	*1 Gram Anhydrous Thiosulfate Dissolves*					
	Valenta			*Busch*		
	AgCl	*AgBr*	*AgI*	*AgCl*	*AgBr*	*AgI*
10	0.635	0.555	0.0524	..	..	..
50	0.660	0.627	0.0495	0.593	0.525	0.043
100	0.708	0.604	0.0518	0.562	..	..
150	0.677	0.508	0.0481	..	0.491	0.038
200	0.575	0.546	0.0565	..	..	..

The ratios between the chloride, bromide, and iodide are approximately those to be expected in view of the relations between the respective solubility products and the fact that the complex ions undergo a slight dissociation, producing a few free silver ions. The concentration of these free ions is proportional to that of the complex ions and inversely proportional to that of the excess thiosulfate ions; it is definitely limited by the concentration of halide ions and the solubility product of the corresponding silver halide. In this manner, the total concentration of silver for a given thiosulfate concentration is limited by the nature and concentration of the halide ions present. This has been demonstrated by several investigators,[9,15] who showed that an excess of the halide ion depressed the solubility of the silver halide.* Since the majority of photographic emulsions contains mixtures of the silver halides, the effect of them upon one another, as evidenced by the solubilities of mixtures, is of importance. Busch[15] investigated this point and found that, in mixtures of silver bromide and silver chloride, the decrease in solubility varies directly with the bromide concentration, or the solubility shows a linear variation as the proportions are varied between pure chloride and pure bromide. In mixtures of either of these salts and silver iodide, on the other hand, the presence of a small percentage of iodide greatly depresses the solubility, while an increase in the iodide concentration has proportionately less effect.

In practice, the life of a fixing bath is definitely limited to a silver halide concentration considerably below that required for saturation because of the tendency of the complex silver salts to become adsorbed to the gelatin or silver grains of the image. These adsorbed complexes are not readily washed out and so remain in the film, where they later decompose and cause stain. The tendency for the complex salts to be adsorbed seems to be greater in acid than in neutral baths so that in fixing power acid baths are less efficient than plain solutions of thiosulfate. Practically, this is of little importance because other factors, such as an increase in the time of fixation or the loss of hardening properties, usually terminate the usefulness of the bath before this concentration is reached.

Thiosulfate, to some extent, will attack metallic silver, especially if it is in a very finely divided form. Thus, the image of a print will be attacked by an aerated fixing bath, especially if the pH is low.[16a] This was shown by Eggert and Noddack,[16b] who greatly decreased the effect of thiosulfate on the image by the addition of alkali. In post-fixation development, this effect is of primary importance (Chapter VIII, p. 307). The attack on silver appears to be due to dissolved oxygen. The maximum rate of reduction is obtained in a 5 to 10 per cent concentration of the sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$). The oxidizing agent could also be sulfur dioxide, which is present in highly acid sulfite solutions and which may form complex compounds with the constituents. Whether the formation of such compounds is only incidental or is essential to the reduction is not definitely established. Chemical studies of the oxidizing properties of sulfur dioxide in acid solution toward multivalent elements, such as iron, copper, mercury, and molybdenum, have been made by Smythe and Wardlaw [17] and collaborators, and also by Carter [18] and others. It appears that in such reactions the sulfur undergoes reduction to a lower valence state which may be analogous to the formation of hydrosulfite (as in $Na_2S_2O_4$).

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* This is true until relatively high concentrations of the halide ions are reached; they then increase the solubility owing to the formation of complex silver halide ions.

If the silver is removed from a negative by means of an oxidizing agent, such as ferricyanide and bromide, followed by fixation, a faint image remains. This was shown by Lumière and Seyewetz [19] and Lüppo-Cramer [20] to consist of silver sulfide. Ross and Crabtree [21] found that the addition of sufficient iodide to the fixing bath avoided the production of the silver sulfide image upon reduction of the washed film in Farmer's reducer. It can be shown that this regression of the silver sulfide image is progressive as the concentration of iodide in the fixing bath is increased. Reindorp [22] investigated the origin of the silver sulfide and found that silver chloride emulsions gave the residual image, while some silver bromide emulsions did not. He identified the residual image as silver sulfide and found that the Hickman-Weyerts method of optical intensification (Ch. XIV, p. 555) with sodium-silver sulfite solutions gave deposition on the residual image. He attributed the formation of the silver sulfide to the instability of the sodium silver thiosulfate complexes rich in silver and concluded that the silver sulfide was formed during fixing. His explanation cannot be regarded as conclusive, but the tendency toward silver sulfide residual images seems to be closely related to the solubility and rate of solution of the silver halide.

RATE OF FIXATION

In the solubility investigations, the determinations were made not with photographic emulsions but with the silver salts alone. With actual emulsions, the rate of fixation is of much more practical importance than the total solubility of the silver halides and is affected by a number of other physical and chemical factors. This is obvious if the three main steps of the process are considered: (1) The diffusion of the fixing agent into the emulsion, (2) the solution of the silver halide grains, and (3) the diffusion of the complex silver-bearing ions from the emulsion.

Sheppard and Mees[23] investigated the effect on the rate of fixation of a number of factors, such as concentration of the bath, rate of stirring, and hardening of the emulsion. Their results showed that the rate is governed by the physical processes, such as diffusion, rather than by the much more rapid chemical reactions. The course of the fixation reaction was followed by determining photometrically the solid silver halide remaining in the emulsion at various times throughout the course of fixation. To prevent darkening of the emulsion during measurement, a yellow filter was used to cut off the blue and violet light. If D_0 is the original density and D that at any time t, $1 - D/D_0$ is the fraction of the total silver halide dissolved; and this plotted against time gives the velocity curve of fixation. The results for the various concentrations of thiosulfate, much lower than those used in practice, are given as curves in Figure 138. If x is the amount of silver bromide dissolved, $\frac{dx}{dt}$ increases at first and then becomes constant, *i.e.*, $\frac{dx}{dt} = F$, or, integrated, $x = Ft + B$ if the rate of solution is constant. F is the slope of the straight-line portions of the curves and B the intercept of the straight-line portion (extended) with the time axis. Table LVI shows that F is directly proportional, and B inversely proportional, to the concentration. The presence of N/10 potassium bromide was found to have no influence on the rate of fixation. This concentration of bromide ions is not large enough to compete effectively with the much greater tendency of the silver ions to form complex ions with thiosulfate and could not affect the equilibrium concentration of the silver ions in solution

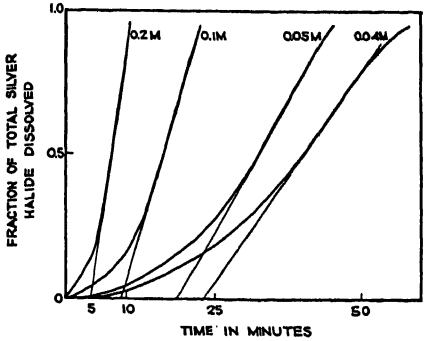

Fig. 138. Velocity curve of fixation.

TABLE LVI

RELATION BETWEEN RATE OF FIXATION AND CONCENTRATION OF THIOSULFATE

Concentration $Na_2S_2O_3$ *C*	*As Grams per Liter of Thiosulfate (Approx.)*	*F*	$\frac{F}{C}$	*B (Minutes)*	*B* × *C*
0.20 M	50	7.3	36	4	0.8
0.10 M	25	3.5	35	9	0.9
0.05 M	12.5	1.8	36	18	0.9
0.04 M	10	1.5	37	23	0.9

and, consequently, the rate of solution. But the rate of solution would also be affected if the establishment of equilibrium for complex-ion formation were slow compared with the instantaneous adjustment between silver ions and bromide ions. The silver-ion concentration and, accordingly, the rate of solution, would then be determined as follows:

$$[Ag^+][Br^-] = K,$$

$$[Ag^+] = \frac{K}{[Br^-]};$$

and the rate of solution would be inversely proportional to the bromide-ion concentration. Since both the reactions in solution occur instantaneously, the rate of the reaction is determined by the heterogeneous factors: the dissolving power of the solution, the surface of the solute, and the diffusion of the components. This is expressed by the equation

$$\frac{dx}{dt} = k\frac{(a - x)DS}{d},$$

in which S is the surface of the solid substance; D, the diffusion coefficient of the reacting salt; d, the diffusion path; a, the initial concentration; and x, the equivalent of solid dissolved in time t. If a is large with respect to x, as in fixation, this will become

$$\frac{dx}{dt} = k\frac{a \cdot D \cdot S}{d} = \text{constant},$$

as found experimentally. The increase of $\frac{dx}{dt}$ in the first stage of fixation is explained by Sheppard and Mees by the fact, observed microscopically, that the surface layers of the emulsion are somewhat poor in halide, probably in consequence of sedimentation, assisted possibly by surface-tension phenomena. Sheppard has since suggested that swelling, by changing the diffusion path *d*, may have some effect.

All of these results were obtained while the plate remained motionless in the solution. If the diffusion velocity is a controlling factor in the rate of fixation, stirring of the solution should increase it. This was found to be so, as shown by Figure 139, and the induction period is shortened also. After some time, the rate apparently becomes proportional to the total mass or density of silver halide present, fixation following an exponential function

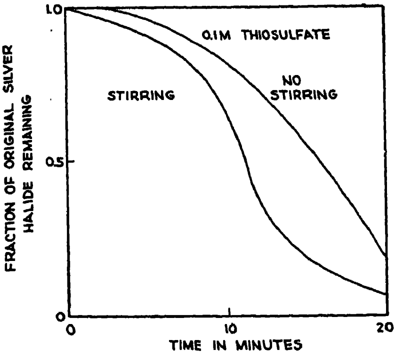

FIG. 139. Effect of stirring on the rate of fixation.

$$\frac{dx}{dt} = k(a - x).$$

Warwick,[21] using a colorimetric method to determine the amount of silver reaching the external solution during definite time intervals, also concluded that the action follows an exponential form or that, during equal intervals throughout its course, the fixation removes a constant fraction of the silver halide present at the beginning of the interval.

These methods made it possible to follow the course of fixation and thus to discover the nature of the reaction and the controlling factors. In practice, however, the greatest interest lies in the determination of the time required to complete the fixation of a material with a given concentration of sodium thiosulfate and, in the determination of the optimum concentration, to give complete fixation in the shortest time. This can be done quite easily by measurement of the clearing time or that required for the disappearance of the last visible traces of the silver halide.

In most of the work done on the rate of fixation, only this value has been determined.

The clearing time, or the practical rate of fixation, is affected by the following factors and probably by others more obscure:

1. Nature of emulsion.
2. Thiosulfate concentration.
3. Nature of the thiosulfate cation.
4. Temperature.
5. Agitation.
6. Degree of exhaustion.
7. Presence of other salts.

1. Nature of Emulsion

The clearing time varies to some extent with the silver halide content of the emulsion and the composition of the halides and is very dependent on the grain size, being much shorter for fine-grain than coarse-grain emulsions because of the much greater total area of the fine grains. This is illustrated in Figure 140,

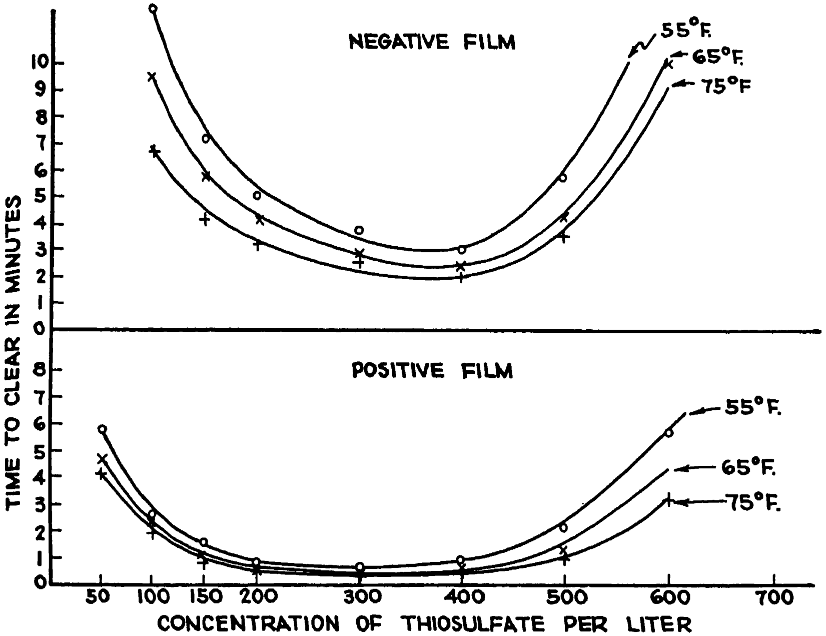

FIG. 140. Clearing times for motion-picture negative film above and positive film below.

where the curves for motion-picture positive film are for a comparatively fine-grain emulsion and those for motion-picture negative are for a moderately coarse-grain emulsion. The clearing time varies also with the mean diffusion path in the emulsion and so is longer for thick emulsions than for thin ones. The hardness of the gelatin has very little, if any, effect. Sheppard and Mees [23] could find no difference between an emulsion which melted at 105° F. and one hardened in formalin until it did not melt at 212° F. and, from a comparison with other diffusion processes, showed that this is to be expected.

2. Thiosulfate Concentration

A number of investigators have studied the effect of thiosulfate concentration on the clearing time. The curves in Figure 140, from Crabtree and Hartt,[25] and Figure 141, from Sheppard, Elliott, and Sweet,[5] are typical of the results obtained by these investigators and by Piper,[26] Warwick,[24] Renwick,[27] Strauss,[28] and others. The published data are remarkably concordant, considering the differences in emulsions and other experimental conditions. As the curves show, at low concentrations the clearing time is fairly long but decreases rapidly with increase in thiosulfate concentration up to a certain optimum value, beyond which the clearing time begins to increase. For Eastman Motion Picture Panchromatic Negative film, this minimum occurred at a concentration of 40 per cent thiosulfate, while with Eastman Motion Picture Positive film it occurred at 30 per cent.

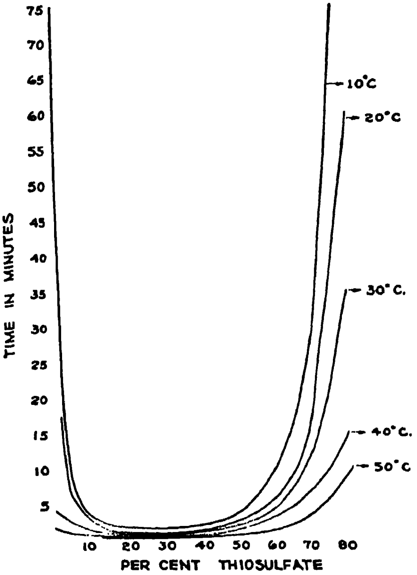

FIG. 141. Effect of thiosulfate concentration on the clearing time.

Sheppard [5] considers that the existence of an optimum concentration (for least time of fixation) is due to the point of balance between increase of diffusion velocity with concentration and decrease of swelling of gelatin with concentration of the thiosulfate solution, as shown in Figure 142.

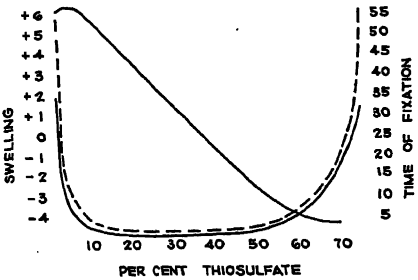

Fig. 142. Effect of thiosulfate concentration on the swelling and clearing time.

3. Nature of the Thiosulfate Cation

As early as 1868, Spiller[29] recommended the use of ammonium thiosulfate in place of sodium thiosulfate because of its more rapid and thorough action. In 1914, Piper[30] investigated the rates of fixation with ammonium, sodium, potassium, and calcium thiosulfates, and found wide variations in the optimum concentrations and in the clearing times at the optimum concentrations, as shown in Table LVII. It is to be noted, however, that when the weight percentages are converted to molar concentrations of thiosulfate, the optimum concentrations become much more nearly equal. Unpublished data obtained in the Kodak Research Laboratories confirm this, indicating that for lithium, ammonium, sodium, potassium, and calcium thiosulfates, the optimum concentrations lie between 1.3 and 1.8 molar, apparently varying as much with the type of emulsion as with the thiosulfate used. Wide differences in the optimum rates were observed for the various thiosulfates.

TABLE LVII

	Clearing Time		*Optimum Clearing at 57° F.*		*Optimum Molar Conc.*
Thiosulfate	*50% Solution*	*15% Solution*	*Time*	*Conc.*	
Calcium	—	—	4 min.	55%	2.1
Sodium	2¾ min.	6 min.	1 min. 55 sec.	40%	1.6
Potassium	—	—	4 min.	30%	1.4
Ammonium	28 min.	1 min. 20 sec.	1 min. 20 sec.	15%	1.0

Because of its more rapid action, a number of investigations have been made on the use of ammonium thiosulfate and the addition of an ammonium salt, such as ammonium chloride, to hypo (sodium thiosulfate) solutions. Lumière and Seyewetz[31] found that, if ammonium chloride equal to one fourth the weight of hypo was added to a 15 per cent hypo solution, the clearing time is considerably shortened, while additions to a 40 per cent hypo solution extend the clearing time. They also investigated the stability of the complexes formed when silver bromide is dissolved in solutions of hypo containing ammonium chloride and found that, in the dry state, these complexes were less stable to light than those formed with plain hypo solutions. They concluded, therefore, that an image fixed in a solution containing ammonium chloride might be more likely to discolor if it was improperly washed after fixation. This has been generally misinterpreted by later writers as proof that images fixed in ammonium thiosulfate or hypo containing ammonium chloride are less stable than images fixed in plain hypo. Experiments in the Kodak Research Laboratories show that this is not the case.

Piper[32] also investigated the effect of adding ammonium chloride to hypo solutions of various concentrations and obtained the curves shown in Figure 143. It is evident that the clearing time is least for a concentration of ammonium chloride very considerably lower than that required to convert all the hypo to ammonium thiosulfate. Lumière and Seyewetz[33] concluded that the addition of ammonium chloride accelerates the rate of fixation only with emulsions containing silver iodide, but other investigators[15,34] have found that ammonium thiosulfate gives more rapid fixation even with pure bromide emulsions, though the advantage is greater with emulsions containing silver iodide. Similar effects have been found with other ammonium salts, but the chloride has been used in most investigations.

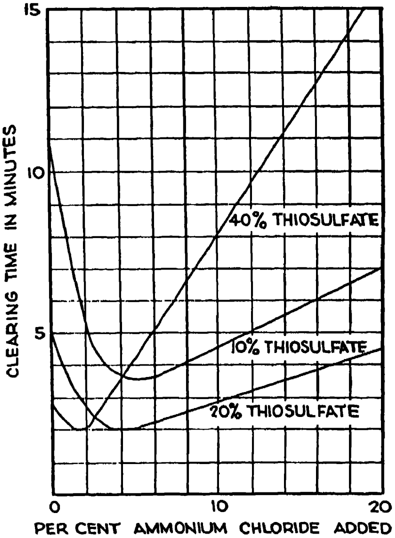

FIG. 143. Effect of ammonium chloride on the clearing time.

4. Temperature

The temperature of the fixing solution has a decided effect on the clearing time. The magnitude of the effect is a pronounced function of the concentration, being a minimum for the most rapid-working concentrations and becoming much greater for concentrations much above or below the optimum. An increase of temperature has evidently a double influence, increasing the swelling of the gelatin and increasing the rate of diffusion. The optimum working temperature appears to lie between 60° and 70° F. Below this range, the action is too slow, while above it the swelling of the gelatin becomes excessive. Where temperatures above 70° F. are unavoidable, it is desirable to add some agent to repress the swelling of the gelatin.

5. Agitation

Since the rate of fixation is controlled by the diffusion into the emulsion of the thiosulfate ions and the diffusion out of the complex silver-bearing ions, agitation increases the rate by supplying fresh solution at the emulsion surface and removing the products from the emulsion surface. This is shown in the following table:

TABLE LVIII

EFFECT OF AGITATION ON TIME TO CLEAR AT 65° F.

Hypo Conc.	*Nature of Film*	*No Agitation*	*Agitation Every 30 Seconds*	*Continuous Agitation*	*Brush Treatment*
35%[a]	Eastman Panchromatic Negative	120 sec.	120 sec.	105 sec.	90 sec.
35%	Eastman Motion-Picture Positive	35 sec.		35 sec.	30 sec.
10%	Eastman Motion-Picture Positive	150 sec.	120 sec.	90 sec.	75 sec.

[a] Crystalline thiosulfate was used. A 35 per cent solution was prepared by dissolving 35 grams in water and adding water to make 100 cc. of solution.

The effect is seen to be more pronounced for the more dilute solutions. If the bath is not agitated, the position of the film in the bath has considerable effect because the differences between the specific gravities of the fresh solution and the reaction products can, in some positions, induce strong convection currents which sweep the emulsion surface.

6. Degree of Exhaustion

As a fixing bath is used, a number of changes take place in its composition. In the first place, hypo is consumed by the formation of the complex silver salts which, with the sodium halides resulting from the reaction, accumulate in the solution. Also, since a small volume of water or developer is carried in by the emulsion of each film while hypo solution is carried out, during the life of the bath a relatively large quantity of water is added and the solution becomes correspondingly diluted. For the usual baths, in which the initial hypo concentration is just below the optimum, all these effects tend to increase the time of fixation, which, therefore, increases fairly rapidly with use and becomes excessive before the actual silver content of the solution is high enough to threaten subsequent discoloration of the film.

7. Presence of Other Salts

The effect of the addition of certain neutral salts to the hypo solution has been noted by a number of investigators. In high concentrations, added salts may act as retardants; but in low concentrations some act as accelerators. Except for ammonium chloride, however, which has been discussed, the degree of acceleration is comparatively slight. The salts of most practical interest are the sodium halides, since they accumulate in the solution as by-products of the fixing reaction. Strauss found that sodium chloride acts as an accelerator, while sodium bromide has some retarding action, although Sheppard and Mees had not detected it at low hypo concentrations; and sodium iodide has a powerful retarding action. Since practically all emulsions, except paper emulsions, contain a small percentage of silver iodide, its effect is of great importance in the most efficient utilization of fixing baths and the re-use of desilvered baths.

TIME FOR COMPLETE FIXATION

Since the ill effects of incomplete or faulty fixation appear only after storage of the image for a considerable time, the importance of proper fixation is often overlooked. This very fact has made it difficult also to determine the point at which fixation may be considered complete. The old photographic rule-of-thumb axiom is that fixing is complete in twice the clearing time. The findings of Warwick[24] and others indicate that this has experimental justification since, at the point of clearing, they found approximately 5 per cent of the original silver halide still in the emulsion. This, they consider, would be sufficient to cause trouble later, while at the end of twice this time there would be only 5 per cent of this quantity, or 0.25 per cent. On the other hand, Lumière and Seyewetz,[35] using the sensitive sulfide test, found that thorough washing removes all silver from the emulsion if fixation is stopped at the moment that all visible traces of the silver halide have disappeared. This result has been confirmed by several others,[36] using widely varying experimental methods.

However, when either plain or acid hardening fixing baths of increasing degrees of exhaustion are used, thorough washing does not remove all silver from the emulsion if fixation is stopped when all visible traces of the silver halide have apparently disappeared even if the time of fixation is increased several times over the time required for disappearance. This apparent mordanting of silver ions by the gelatin may be overcome by the use of a second fresh fixing bath following the partially exhausted bath.

In the case of paper prints, it is necessary to increase the time of fixation greatly beyond double the time required for clearing, because in a partially exhausted fixing bath the complex silver thiosulfates are apparently mordanted to the gelatin or paper fibers[37] and are not readily removed by subsequent washing unless the print is thoroughly fixed. The practice of transferring the prints to a second, fresh bath aids in washing the print free from silver salts.

USEFUL LIFE OF FIXING BATH

As mentioned, the useful fixing capacity of a hypo solution cannot be measured directly by the solubility of silver chloride, bromide, or iodide in the solution. Long before the silver concentration has reached saturation, it is high enough to cause trouble from incomplete removal of the silver compounds from the gelatin during washing. These silver complexes, which are apparently adsorbed to the gelatin, may subsequently decompose, causing discoloration of the image and staining of the film.

It is of importance, therefore, to know the point at which a fixing bath becomes unsafe to use.

Lumière and Seyewetz[8] investigated this problem by dissolving various quantities of silver bromide in thiosulfate solutions, moistening strips of filter paper with them, and exposing the strips to light and air for several days. If the paper discolored, the bath was judged to be unsafe. By this method they obtained the following results:

TABLE LIX

EFFECT OF CONCENTRATION ON USEFUL LIFE OF FIXING BATH

	Silver Bromide Dissolved in 100 cc.		*Equivalent Number of Negs. (9 by 12 cm.) Fixed by 1 Liter Without Subsequent Stain*
Solution	*Saturated*	*Without Subsequent Stain*	
5% Hypo	2.0 grams	1.25 grams	33
15% Hypo	6.3 grams	3.8 grams	100
40% Hypo	20.5 grams	5.0 grams	133
15% Hypo 1.5% Bisulfite Liquor	6.1 grams	1.65 grams	45
15% Hypo 1.5% Bisulfite Liquor 0.5% Alum	5.9 grams	2.20 grams	60

Later, using the sensitive sulfide test to detect silver, they[35] found that a 20 per cent solution of hypo could tolerate only 20 grams of silver bromide per liter, the amount contained in approximately 5000 square centimeters of a negative film material. If the quantity of silver bromide was greater than this, longer treatment in the bath did not remove the residual silver, but the use of a fresh bath effected complete removal. At this concentration of silver bromide, the clearing time was 9 minutes compared with 4 minutes for the fresh bath.

THE ACID FIXING BATH

Inasmuch as the transfer of photographic material from the developer to the fixing bath carries considerable amounts of alkaline developer into the fixing solution, the latter soon becomes discolored with oxidized developer and stains the gelatin layers of the films and papers used. To prevent this and to arrest development rapidly after the material reaches the fixing bath, it is desirable to use an acid solution of thiosulfate. Unfortunately, thiosulfate is unstable in the presence of acids, depositing sulfur, but this reaction can be prevented by the use of sulfite in the solution. An acid fixing bath therefore contains thiosulfate, a weak acid, such as acetic, and sulfite. Lainer's theory[38] of the acid fixing bath, based on preferential decomposition of the sulfite and assumed formation of acid salts, does not appear adequate. A more satisfactory explanation of the protective action of sulfite is derived from the physical chemistry of the decomposition of thiosulfates by acids.

Landolt,[39] in a paper on the "Time of Existence of Thiosulfuric Acid in Aqueous Solutions," concludes among other things that: (1) The nature of the acid employed does not affect the decomposition and (2) the time of stability is independent of excess of thiosulfate or acid. He considers that the "life period" of thiosulfuric acid is measured by the interval between the addition of an acid solution to thiosulfate and the first appearance of a sulfur cloud or opalescence.

This induction period was made the subject of an extensive investigation by von Oettingen.[40] He did not accept the conception of a definite "life period" of the thiosulfuric acid as the cause of the induction but regarded it as due to a supersaturation of the solution with sulfur, which he supposed to pass through a metastable limit before precipitation occurred. He also considered that the reactions were between ions, the actual reaction taking place between the thiosulfate ion and the hydrogen ion from the acid according to the equation

$$S_2O_3^{--} + H^+ \rightleftharpoons HSO_3^- + S. \tag{7}$$

According to this, neither the sodium ion nor the acid anion takes part in the reaction; thus, the nature of the acid does not affect the decomposition unless it has a different dissociation constant. The concentration of the acid, however, has a marked effect, as von Oettingen, contrary to Landolt, found. The inhibiting action of sulfite for the decomposition of thiosulfate, according to von Oettingen, is due to the fact that the reaction is reversible; so that the action of sulfite is due to its mass action in increasing the reverse reaction. Qualitatively, this agrees with the production of thiosulfate from sulfite and sulfur. In attempting to determine the equilibrium conditions for this reaction, Colefax[41] found that disturbing side reactions occur; *e.g.*,

$$2\,Na_2S_2O_3 + 3\,SO_2 = 2\,Na_2S_3O_6 + S. \tag{8}$$

Foussereau[42] followed the decomposition by conductivity measurements. For dilute mixtures of thiosulfate and acid, the curves showing the change of conductance with time have decided inflection points. This he attributed to supersaturation of sulfur and autocatalysis by primary sulfur nuclei. He confirmed this by abbreviating the induction by the addition of partly decomposed solutions.

The fact that in acid decomposition thiosulfate does not change quantitatively to sulfite and sulfur is shown by the fact that the iodine titration value, which should double for complete reaction, actually only increases by 80 or 85 per cent. It was shown early that small quantities of polythionates are formed.[43] Bassett and Durrant,[44] after extensive experiments and a comprehensive consideration of the results of other investigators, in a paper on "The Inter-relationships of the Sulfur Acids," concluded that thiosulfuric acid, in the range of acidity encountered in fixing baths, decomposes in two ways, according to the equations

$$2\,H_2S_2O_3 \rightleftharpoons 2\,H_2SO_3 + S_2 \tag{9}$$

and

$$2\,H_2S_2O_3 \rightleftharpoons H_2S + H_2S_3O_6. \tag{10}$$

Since sulfurous acid is much weaker than thiosulfuric acid, both of these reactions correspond to a definite decrease of hydrogen-ion concentration in proceeding from left to right. They tend to occur in acid solution, therefore, and to be reversed in alkaline solution. Normally, reaction (9) occurs to the greater extent, reaction (10) proceeding much more slowly. The authors consider that the hydrogen sulfide immediately reacts with excess sulfurous acid, with eventual formation of sulfur. Also, part of the trithionate formed by reaction (10) probably reacts with the sulfur to form tetrathionate and pentathionate. The inhibiting action of sulfite in acid solution seems, therefore, to be due to its mass action effect in reducing the velocity of the reaction to the right in equation (9), thus allowing the products of the much slower reaction (10) more chance to react with the sulfur formed, and thus keeping its concentration longer below the precipitation limit. The precipitation of the sulfur is probably determined to a considerable extent by colloid chemical considerations, such as the influence of the electrolytes present on the stability and coagulation of the sulfur hydrosol.

CONTROL OF HYDROGEN-ION CONCENTRATION

It is evident from the considerations discussed that, for a given quantity of sulfite, the desirable maximum of which is limited by several factors, there is an upper limit to the permissible hydrogen-ion concentration, beyond which the protective action of the sulfite would be insufficient to prevent early precipitation of sulfur. On the other hand, the concentration of hydrogen ion must be above a certain lower limit for the bath to act as an acid fixing bath, preventing the formation of stains or dichroic fog by neutralizing the alkali of the developer. Also, if the bath contains alum or other hardening agents, the permissible range of hydrogen-ion concentration may be further limited by effects on the hardening action. A large total or reserve acidity is desirable, however, so that the bath can neutralize a considerable quantity of developer solution and to avoid the necessity for discarding it long before its fixing power is exhausted.

These two conditions can be met only if the solution exhibits considerable resistance to change of hydrogen-ion concentration when it is subjected to gain or loss of acid or alkali.[45] The magnitude of the buffer action of a given solution is determined by the interrelationships of the component compounds and their various dissociation products. It can be raised to considerable proportions over a given small range of hydrogen-ion concentration by the proper selection of compounds and adjustment of their concentrations.

In a potassium alum hardening fixing bath containing boric acid,[45] to prevent sulfurization on the one hand and sludging on the other, the pH should remain within the range of 4.0 to 6.5 throughout its life. It is not essential that the bath be buffered over the entire pH range from 4.0 to 6.5, which would require the presence of several acids, each producing buffer action over portions of the pH range.

Theoretically, at least, the only essential for a satisfactory fixing bath is a high concentration of an acid which does not affect the hardening or sludging properties of the bath and which has a dissociation constant preferably between a value of 3×10^{-5} and 10^{-6} and sufficient alkali or salt of the acid to produce a bath with an initial pH value greater than 4.0. A considerable number of acids within these limits can be found in tables of dissociation constants; but, if practical and economic factors are considered, acetic acid is the most generally useful.

WASHING

Washing operations are used in photographic processing to remove reagents which might affect later reactions adversely, and at the end of processing to eliminate all soluble compounds which might impair the stability of the photograph. The common purpose of final washing is to remove the fixing salts which are contaminated with dissolved silver compounds in the form of complexes with thiosulfate. Failure to remove the silver compounds eventually causes stain in the highlights and unexposed areas, while if thiosulfate and its oxidation product tetrathionate are not eliminated, there will be a slow sulfurizing of the image on keeping. Effective washing is especially important when photographs are to be kept as records.

The theory of photographic washing is treated in a number of papers, the most important being those of Elsden,[46] Warwick,[47] and Hickman and Spencer.[36b, 48]

Thiosulfate diffuses from a plain gelatin film during washing as from a layer of still water, with little resistance and without appreciable adsorption to the gelatin. If a silver image is present, there appears to be relatively little adsorption to the silver. Several factors, however, affect the rate at which the thiosulfate diffuses from the layer, such as the use of a separate hardening bath or a fixing solution containing hardening agents, and temperature has a marked influence. The diffusing away of the thiosulfate is a simple exponential process such that, as time progresses, the amount leaving decreases geometrically. Stated in another form, the thiosulfate leaving at any moment bears a constant ratio to the quantity remaining in the film at that moment. The quantity of thiosulfate, M, washing out of the a film in a period of t minutes from the start is given by

$$\frac{dM}{dt} = k(A - M),$$

where k is the elimination constant of the film and A is the thiosulfate originally present, whence

$$k = \frac{1}{t} \log \frac{A}{A - M} \cdot$$

A more convenient equation deduced from the above is

$$k = \frac{1}{t_2 - t_1} \log \left(\frac{\text{Concentration at time } t_1}{\text{Concentration at time } t_2} \right) \cdot$$

The concentration at times t_2 and t_1 may be found experimentally by analysis using (1) mercuric chloride for film and (2) silver nitrate in the case of prints.[37] These methods measure quantitatively the amount of thiosulfate remaining in the film or print, respectively, and are usually more accurate than the titration of the salt in the film with iodine or measurement of the electrical conductivity of the wash water itself.

The experimental procedure for film is to place one square inch in 10 cc. of a solution containing 25 grams of mercuric chloride and 25 grams of potassium bromide per liter, leave the film sample in this for 15 minutes with frequent agitation, and compare the resultant turbidity with that produced in a series of standard solutions of thiosulfate in the reagent.[49] The method is specific for thiosulfate and measures quantities as low as 0.005 milligram per square inch. The silver nitrate test is described in the discussion on the washing of papers.

The numerical value of the constant k does not convey as much to the imagination as the "half-period," *i.e.*, the time required for the concentration in the film to diminish to one half. For emulsions coated on glass or film base, this varies between 10 and 40 seconds for the most extreme varieties if washing is properly done. Emulsions on paper behave differently and are discussed later. If the half-period is, say, 30 seconds, in three minutes the salt content of the emulsion layer falls to 2^{-6}, or less than 2 per cent of its initial value; in six minutes, to 2 per cent of 2 per cent, which is four parts in 10,000, a very small quantity.

A time of six minutes contrasts strongly with the time of washing decreed by custom and the manufacturer's instructions. The discrepancy lies, of course, in the subsidiary factors of stirring and water changing.

The ideal formula for the rate of elimination presupposes that the thiosulfate diffuses from the gelatin layer into pure water. In practice, if a plate or film containing thiosulfate is allowed to rest undisturbed in a tray of water, the thiosulfate will diffuse out and will form a layer of relatively high concentration at the emulsion surface; this will slowly pass into the bulk of the water until such a concentration is reached that there is a balance, and some thiosulfate will remain in the layer. This concentration will naturally depend upon the volume of water. For the maximum effectiveness of elimination, therefore, there must be a constant renewal of fresh water at the emulsion surface. This is accomplished by the material being transferred to fresh water at frequent intervals or a running stream of fresh water being used.

It is desirable to examine the subject of exponential dilution further. A vessel holding one liter, if drained of its contents, retains about 5 cc. wetting the sides. Refilling disperses the 5 cc. in a second liter of fresh water, giving a concentration of 1/200 of the original. If the vessel is drained a second time and refilled, the concentration will fall to 1/200 of 1/200, or one part in 40,000, in a manner exactly analogous to the washing of the emulsion. As the number of changes proceeds arithmetically, the concentration falls geometrically, the factor in this case being 1/200.

Another important example is that in which water enters the vessel continuously and flows to waste at the same rate, so that a constant level is maintained. In a hypothetical case, in which each particle of water as it enters is thoroughly mixed and stirred with that in the tank, the dilution after the passage of a volume equal to that of the vessel is to one half. This is the natural rate of dilution in any vessel to which the water is admitted under sufficient pressure to give vigorous agitation. With the water-changing capacity of this theoretical system taken as *unity*, it can be compared with the factors of various washing devices used by photographers. In the case of a tray in a sink, with water entering at one corner, if the overflow is at the point farthest from the feed, the factor is usually less than unity. If the tray is tilted in the opposite direction, it will be greater, *i.e.*, it will take longer to change the water. Tanks fitted with siphons which drain fluid continuously from the bottom generally have a good water-changing capacity if the incoming water can be prevented from mixing with that already

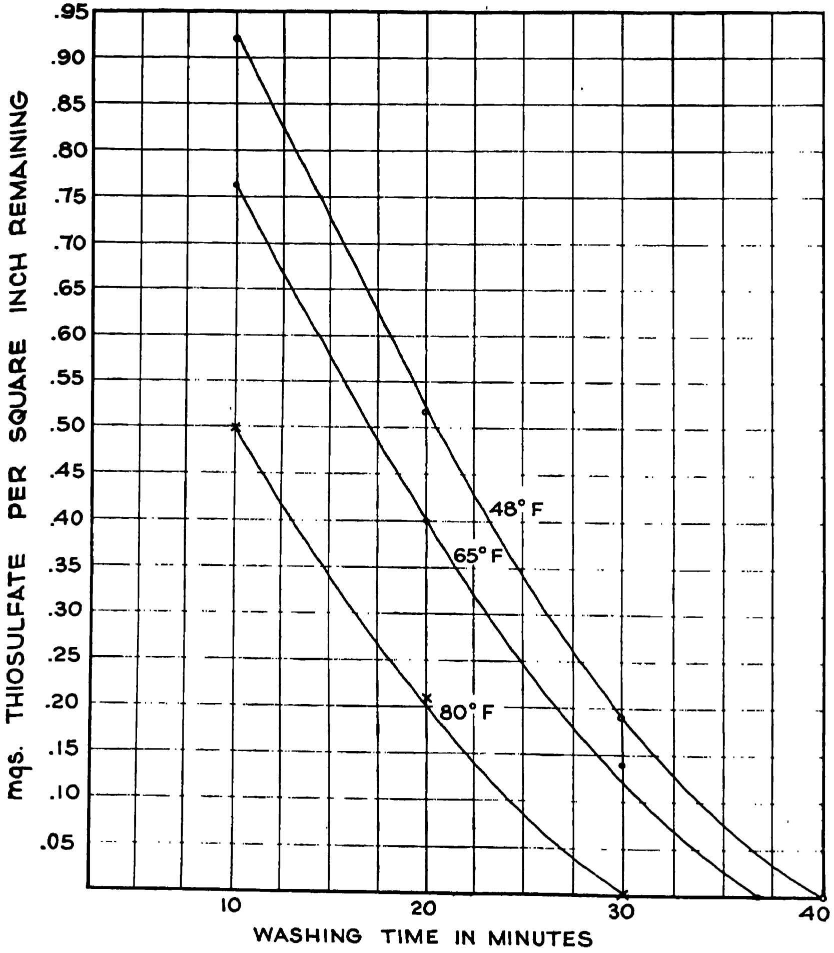

FIG. 144. Effect of temperature on the elimination of thiosulfate from film by washing.

in the vessel. The turbulence is low, however, and the viscous layer of diffused thiosulfate in contact with the emulsion is not washed away, so that little advantage is gained. Syphon tanks which function intermittently and empty completely show the smallest factor and the greatest renewal capacity, but they suffer from the disadvantage that the material is left uncovered for part of the time.

In general, the choice of washing apparatus is unimportant provided that two simple rules are obeyed: The volume of the wash water should be the least necessary to cover the materials; and it should be changed frequently by complete draining or vigorous, continuous flow.

Even with satisfactory washing apparatus, the other factors already mentioned which enter into the determination of the rate of elimination are the temperature of the wash water and the composition of the fixing bath. The effect of temperature is shown in Figure 144. The temperature is in practice limited by the danger of swelling and softening the gelatin. Temperatures of 60°–70° F. are best. For any particular set of washing conditions, thiosulfate is more readily removed from film fixed in a non-hardening fixing bath than from that fixed in a potassium alum-thiosulfate fixing bath, while if a chrome alum fixing bath is used, the elimination will be almost as rapid as with a non-hardening fixing bath.

WASHING PAPERS

Paper prints do not lose thiosulfate exponentially in water. An initial rapid diffusion, which is almost logarithmic, soon degenerates into a very sluggish process. The main bulk of the salt comes out in five minutes, leaving a harmful residue, which may require from ten minutes' to an hour and a half's further soaking. The last traces in many cases cannot be removed by prolonged washing.

The paper fibers retain so much more salt than the emulsion layer that the influence of the latter on the washing time need not be considered. Experiments show that the retention is in the nature of friction, rather than adsorption. The elimination of the salt is retarded by passing through a succession of cell walls, often protected by sizing materials, and is not able to proceed as freely as in a layer of still water. The slower diffusion, as washing progresses, is probably due to differences in the rate of escape from different units in the paper structure. Long after the main bulk of the salt has been eliminated, a small amount continues to percolate from the thick cells or cavities which have been specially protected by sizing. Very minute residues, of the order of 0.03 milligram per square inch, may not wash out in twenty hours.

The rate of elimination from paper prints is affected also by (*a*) the temperature of the wash water and (*b*) the composition of the fixing bath.

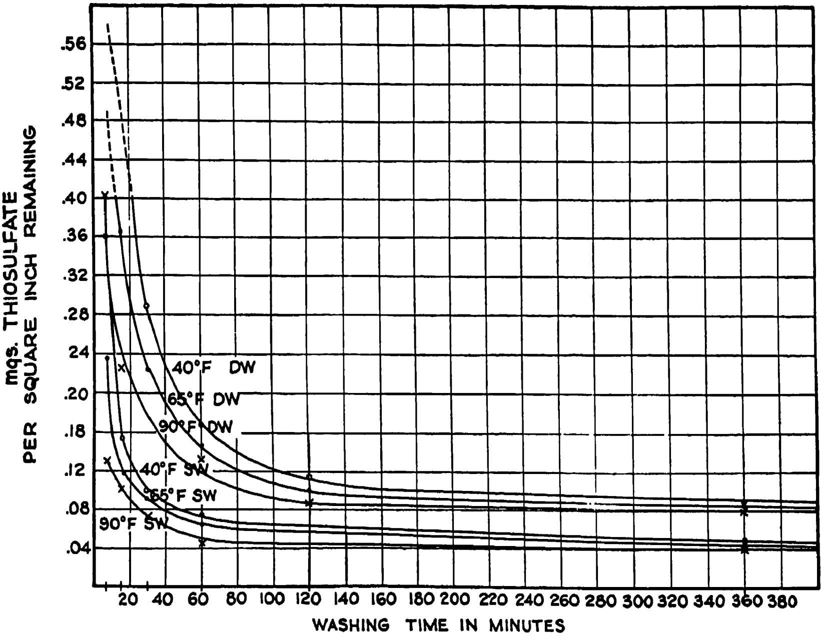

FIG. 145. Effect of temperature on the elimination of thiosulfate from prints: S.W., single-weight paper; D.W., double-weight paper.

Typical washing curves of prints on single- and double-weight paper for different temperatures are shown in Figure 145. The rate of washing increases with the temperature, but for longer times, the rate tends to approach zero. Washing is notably faster with single-weight than double-weight papers. The rate of elimination increases appreciably if prints are fixed in non-hardening or chrome alum fixing baths rather than potassium alum fixing baths.

The concentrations of thiosulfate at times t_2 and t_1, in the formula for the determination of the elimination constant, k (p. 532), are obtained by measuring the thiosulfate retained in the print itself. It is converted into silver sulfide by treatment with silver nitrate, and the density of color produced by the sulfide is determined. Hickman and Spencer [50] showed that the elimination curves have different shapes, according to whether they refer to the raw-paper base, the baryta-coated paper, or the emulsion-coated paper. Thus, in Figure 146, curve *A* gives the thiosulfate remaining after washing for the paper base; *B*, for baryta-coated paper, and *C*, for emulsion-coated paper. The figures on the curves are the weight of anhydrous thiosulfate in the paper (14 square inches) before washing.

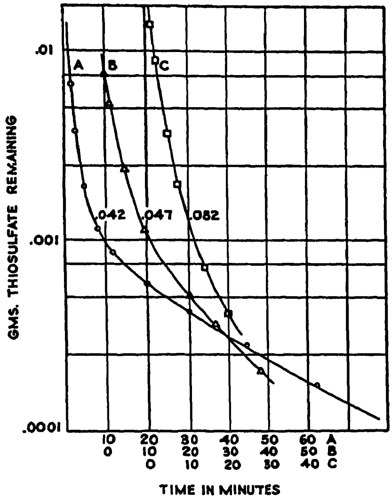

FIG. 146. Elimination curves for (*A*) paper base; (*B*) baryta coated paper; (*C*) emulsion coated paper.

That the nature of the washing curve is due to the structure of the paper as a manufactured sheet, rather than to the constituent fibers, is shown by the fact that stressing the surface or scrubbing or soaking the sheet in a solution which disrupts its texture quickens washing. Figure 147 illustrates the acceleration of washing after treatment with boiling acidified water, which ruptures the sizing.[50]

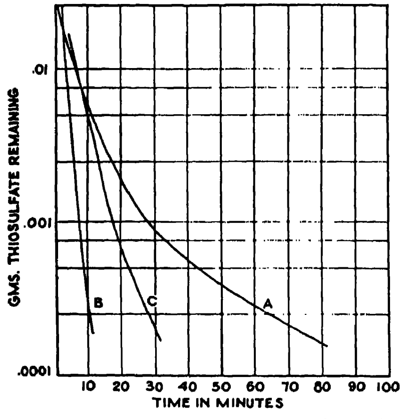

FIG. 147. Acceleration of washing of paper base after treatment with boiling, acidified water: (*A*) normal curve; (*B*) after boiling with hydrochloric acid; (*C*) after boiling with water.

Strong caustic solution has a similar effect. Transferring the thick paper from one bath to another, especially with a rinse between, subjects the paper to disruptive osmotic forces and induces quicker washing. The washing of thick•card may be accelerated rather than retarded by re-immersion in the fixer after a couple of minutes' washing. A final washing removes more salt in half an hour than would come out in an hour without the intermediate treatment.

The permanence of the silver image is governed by the amount of residual thiosulfate present, which under appropriate conditions of temperature and humidity may cause sulfiding of the image. If it is not possible to wash out all of the thiosulfate, as in the case of prints, so-called *hypo eliminators* should be used. These are solutions which oxidize the thiosulfate to a harmless chemical or which assist its elimination by washing. Many eliminators have been proposed, but most of them are ineffective. In 1940, Crabtree, Eaton, and Muehler[37] disclosed improved methods of thiosulfate elimination. Alkalis used alone are most effective for films and plates. After the negatives are washed for about 10 minutes, they are bathed in 0.3 per cent ammonia for 3 minutes and washed for a further 3 minutes. For prints, a solution containing a low concentration of ammonia and hydrogen peroxide is used between washings, the peroxide oxidizing the thiosulfate to sulfate.

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CHAPTER XIV

REDUCTION AND INTENSIFICATION

Changes in the densities of a developed image are sometimes desirable. The processes used are classified as *reduction* and *intensification,* the former referring to methods by which the optical densities of the image are diminished, and the latter to those by which they are increased. (The term "reduction" is unfortunate because the reactions employed are *oxidations*, and it would be better to refer to the process as "weakening," the term used in most languages other than English.)

Images usually require reduction or intensification because the exposure or development was not correct. The faults which may require correction may be classified as follows:

1. Normal exposure	Underdeveloped Overdeveloped
2. Underexposure	Underdeveloped Normally developed Overdeveloped
3. Overexposure	Underdeveloped Normally developed Overdeveloped

It is apparent that two general types of correction are required; namely, a modification of density *proportional* to that present, and which changes the γ, and a modification of density *independent* of the amount present, and which leaves the γ unchanged. These corrections can be effected, to a certain degree, by a suitable choice of the following methods. None of them, however, gives a final result equal to that obtained by correct exposure and development; their use is an expedient and not a practice.

CLASSIFICATION OF REDUCERS AND INTENSIFIERS

Reducers and intensifiers may be classified into general types, depending upon their relative action on the various densities of the image, as shown by a comparison of the $D \log E$ curve of the treated image with that of the original. The type of reduction or intensification is dependent upon the nature of the solution and, to some extent, the grain size distribution characteristics of the image treated.[1]

REDUCERS

Following the nomenclature of Luther,[2] except for a broader interpretation of sub-proportional action, reduction as shown in Figure 148 is (1) proportional if all the densities of the original

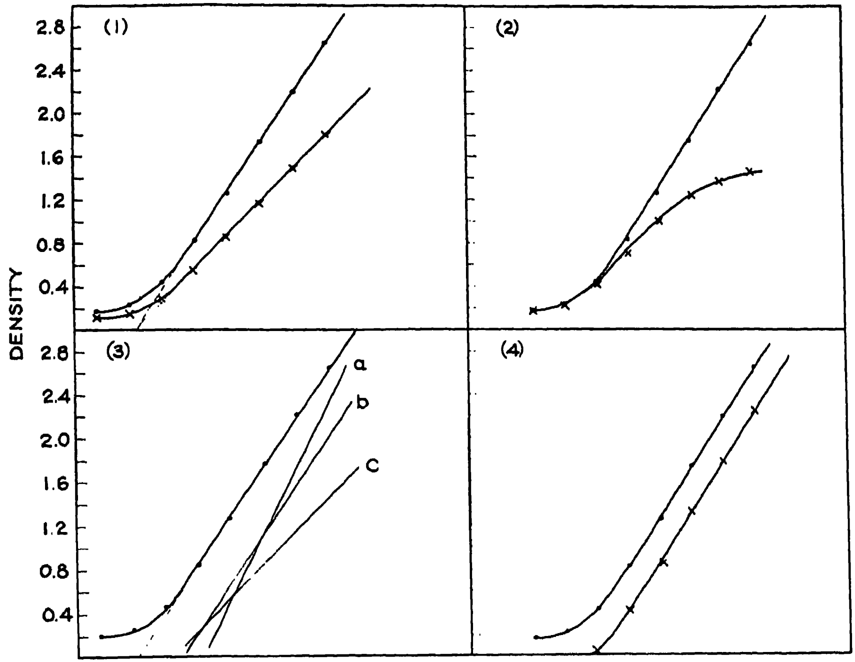

FIG. 148. Various types of reduction: 1, proportional; 2, superproportional; 3, subproportional; 4, subtractive.

are reduced in the same ratio, (2) superproportional if the reduction ratio for the higher densities is greater than that for the lower ones, and (3) subproportional if the reduction ratio for the lower densities is greater than that for the higher ones. (4) Subtractive reduction is a special case of (3), where removal of density is approximately equal from all densities. The term "subproportional" is seldom used since all known reducers of this type approach subtractive action as a limit. Such solutions are sometimes described as *cutting reducers.*

A number of the better-known reducers may be classified as follows:

1. Proportional Reducers
    - Potassium permanganate (alone[3] or with weak acid[4])
    - Permanganate-persulfate with sulfuric acid[5]
    - Ferric ammonium sulfate with sulfuric acid[6]
    - Quinone with sulfuric acid[6d]
2. Superproportional Reducers
    - Ammonium[7] or potassium persulfate[8] alone or with sulfuric acid
    - Ferricyanide-bromide bleach; nonstaining partial redevelopment followed by fixing[9]
    - Bichromate-potassium bromide-hydrochloric acid* bleach; nonstaining partial redevelopment followed by fixing[10]
3. Subproportional Reducers
    - Ferricyanide-thiosulfate (Farmer's)[11,1]
    - Ferricyanide-thiocyanate (Haddon's)[12]
    - Iodine-cyanide[1]
    - Ferric chloride-acid-oxalate-thiosulfate (Belitski)[13]
    - Permanganate-sulfuric acid[1,4c]
    - Bichromate-sulfuric acid[1,4c]
    - Ceric salts with nitric or sulfuric acid[12b,14]

All reducers are oxidizing solutions. They must either oxidize the silver to a soluble salt or contain a solvent for the silver salts which are insoluble in water. Thus, the permanganate, bichromate, ferric ammonium sulfate, ceric, and persulfate reducers are used in the presence of sulfuric acid and dissolve the silver as silver sulfate. Thiosulfate or thiocyanate is used with ferricyanide to dissolve the silver ferrocyanide which is formed; with iodine, cyanide is used to dissolve the silver iodide.

The vigorously acting solution of ferricyanide and thiosulfate, as well as many other subproportional reducers, removes density in almost equal increments from both low and high densities, but generally there is a tendency to remove somewhat more from the denser portions. The latter propensity is greatest for images having a wide range of grain size distribution, as in high-speed negative materials. Upon emulsions having a relatively narrow range of grain size (process and positive), the action of the reducer approaches the pure subtractive.[16] Dilution of subtractive reducers or lowering the concentration of an ingredient often causes the solution to give more nearly proportional action. For the screen negatives used in photoengraving, mixtures having a high concentration of thiosulfate permit preferential reduction of low density edges of half-tone dot images and the smallest dot images, thus "sharpening" the dot edge and increasing the contrast. In this case, diffusion plays an important part in controlling the removal of partially used solution and replenishment with fresh. The ferricyanide-thiosulfate solutions are not stable; some of the thiosulfate is oxidized by the ferricyanide, and other side reactions take place. As indicated by Crabtree and Muehler,[16] the useful life of the solution can be increased many times by the use of sufficient alkali.

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* With relatively low acid content, the lowest densities are intensified; with sulfuric or other sufficiently strong acid, the lower densities are not intensified.

Other nonacid subtractive reducers employ iodine, potassium ferricyanide, and copper compounds as oxidizing agents, together with solvents for silver compounds, such as potassium cyanide, alkali thiocyanates, thiourea, and ammonia. Iodine is used with compounds capable of dissolving silver iodide; for example, potassium iodide or cyanide.

Permanganates and bichromates in sulfuric and nitric acids are also subproportional (subtractive) reducers. Their action is so rapid that they are often employed in reversal processes to remove the silver produced by first development. The equation for the action on silver of potassium permanganate, with sufficient acid to form the neutral sulfate, is typical and may be written

$$10Ag + 2KMnO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Ag_2SO_4 + 8H_2O$$

or ionically:

$$(MnO_4)^- + 5Ag + 8H^+ \rightarrow 5Ag^+ + Mn^{++} + 4H_2O.$$

Silver solution is also brought about by the soluble salts of elements which merely change their valency by a single unit.

Such a change is the passage of ceric sulfate to cerous sulfate:

$$2Ce(SO_4)_2 + 2Ag \rightarrow Ag_2SO_4 + Ce_2(SO_4)_3$$

or

$$Ce^{++++} + Ag \rightarrow Ag^{+} + Ce^{+++}.$$

A practical difficulty in the use of the ceric salts is the ease with which they are precipitated as basic compounds, so that they generally require the presence of additional strong acid.

The reactions of the solutions used as reducers for the silver image do not seem to have been studied adequately. Acidified permanganate, for instance, when it reacts with precipitated metallic silver, yields some silver peroxide, and it is possible that its reaction with a developed image is more complicated than is indicated by the equation given above.

Persulfate Reducers. The reaction to which the most study has been devoted is that between silver and the alkaline persulfates. Ammonium persulfate as a photographic reducer was first suggested by Lumière and Seyewetz in 1898.[7a] Textbooks have continued to recommend it, with the caution, however, that its action is uneven and uncertain. It is normally a superproportional reducer which attacks the heavy parts of the image and leaves the low densities scarcely touched. Under certain circumstances, however, it can act proportionally, and this has proved very confusing. A solution of ammonium persulfate has little action on the image at first, but, after a short time, the heavier densities are more and more rapidly eaten away without appreciable reduction occurring in the lighter ones. Lumière and Seyewetz realized at an early date that, though neutral persulfate dissolves pure metallic silver, *i.e.*, attacks a polished silver plate, its action on the photographic image is enormously accelerated by silver ions and acids. They knew that, as the photographic action proceeds, the solution becomes more acid and the reaction quickens autocatalytically.[15] Sheppard[7c,16] and, at about the same time, Higson[7d] showed that the reactions of the persulfate are determined largely by the catalytic action of impurities. The most important are silver, hydrogen, iron, copper, and chloride ions. The first two are products of the action of persulfate on the image. The silver and hydrogen ions liberated after the first few moments of action cause the velocity of the reaction to increase as the ions become more abundant.

Chlorides hinder the action of persulfate in two ways: In minute quantity, they can remove the few silver ions from the lighter densities and leave those in the heavier scarcely diminished, in which case the reduction becomes even more superproportional. On the other hand, the silver ions in the light densities may be completely removed by the washing after fixation, so that chlorides merely diminish their concentration in the dense parts and the reduction is more nearly proportional. The graph shown in Figure 149, taken from Sheppard's second paper, shows that the first condition usually obtains. The addition of silver salts to the persulfate accelerates reduction for all densities and renders it somewhat more proportional for the complete range. This is well brought out in Figure 150, also from Sheppard's paper.

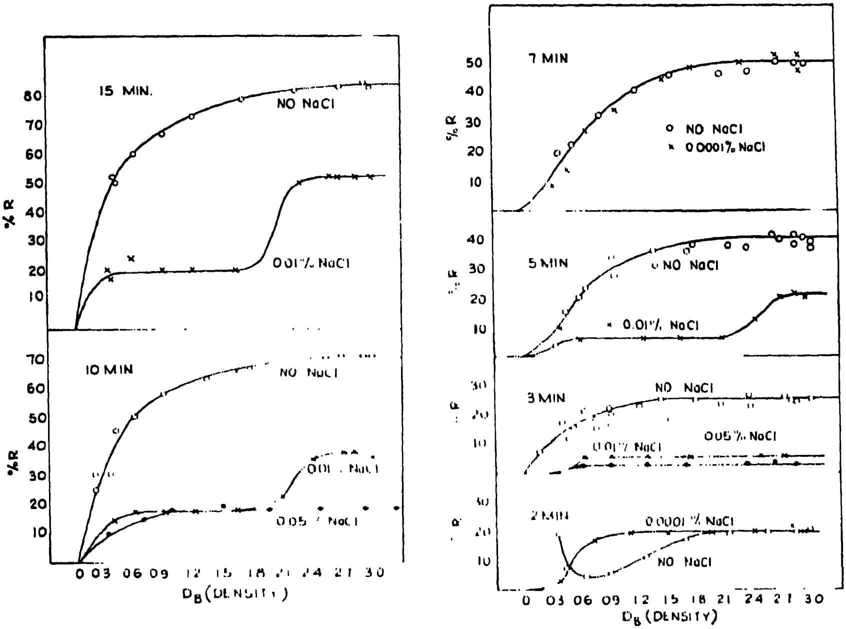

FIG. 149. The effect of soluble chloride on the differential reducing action of persulfate for different times of action.

Higson compiled a bibliography on the subject of persulfate reduction and examined the effect of hydrogen, iron, copper, and chloride ions.[8b] The simple equation

$$2\,Ag + (NH_4)_2S_2O_8 \rightarrow Ag_2SO_4 + (NH_4)_2SO_4$$

cannot represent the actual reaction because the solution grows acid during use. Hydrogen ion accelerates the photographic reduction in apparently the same manner as silver. The chemical equations expressing the oxidation of metallic silver must, therefore, involve the production of both hydrogen and silver ions. Marshall and Inglis,[17] on the one hand, show that persulfate decomposes rapidly in the presence of silver sulfate, and Higson, on the other, that a peroxide or a per-oxy-sulfate of silver is deposited from solution. In the presence of ammonia, the end-products of decomposition are represented by

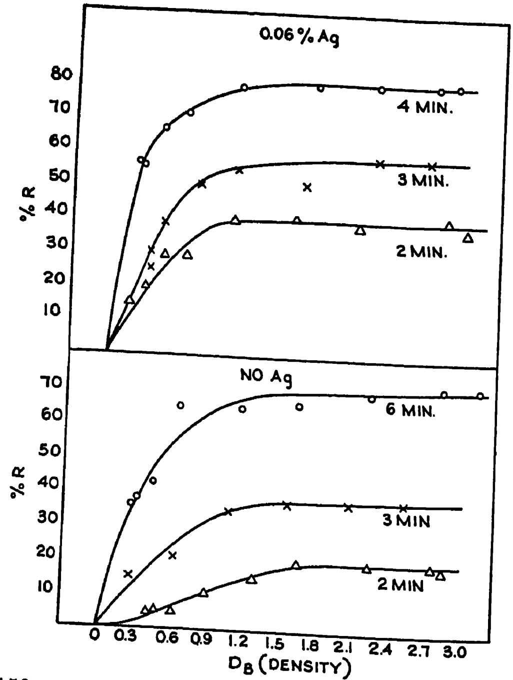

FIG. 150. The effect of silver salts on the differential reduction of persulfate.

$$3\,(NH_4)_2S_2O_8 + 8\,NH_3 \rightarrow 6\,(NH_4)_2SO_4 + N_2,$$

and in acid solution by

$$8\,(NH_4)_2S_2O_8 + 6\,H_2O \rightarrow 7\,(NH_4)_2SO_4 + 9\,H_2SO_4 + 2\,HNO_3.$$

In this case, ammonia is oxidized to nitric acid. This may be ascribed to a decomposition of silver persulfate to form silver peroxide, which has been found experimentally.

$$Ag_2S_2O_8 + 2\,H_2O \rightarrow Ag_2O_2 + 2\,H_2SO_4.$$

Unstable peroxides of this type are powerful oxidizing agents in the presence of acid in a degree roughly proportional to its concentration. The sulfuric acid attacks the peroxide,

$$Ag_2O_2 + H_2SO_4 \rightarrow Ag_2SO_4 + H_2O + O.$$

The nascent oxygen may attack the NH_4 group and form nitrogen or nitric acid. In moderately ammoniacal solution, the reaction is much slower, and silver oxide may be precipitated. During reduction of the photographic plate, the nascent oxygen attacks both the NH_4 group and the silver image, producing both silver and acid, which, in turn, quicken the process. However, even the presence of the ammonium ion is not essential; Higson showed that potassium persulfate also gives superproportional reduction. The conclusions of Sheppard and Higson for the reactions considered show almost complete agreement:

	Sheppard	*Higson*
1.	$S_2O_8'' + H_2O \rightarrow 2HSO_4' + O.$	$S_2O_8'' + H_2O \rightarrow 2HSO_4' + O.$
2.	Atomic oxygen from (1) forms oxides —Ag_2O_2, Ag_2O.	Nascent oxygen from (1) forms peroxide, probably Ag_3O_4.
3.		Silver peroxide oxidizes gelatin and is reduced to Ag_2O.
4.	Oxides, Ag_2O, etc., react with acid $Ag_2O + 2H^+ \rightarrow 2Ag^+ + H_2O$ $2HSO_4^- \rightleftharpoons 2H^+ + 2SO_4^{--}$	Ag_2O reacts with acidic ion HSO_4^-. $Ag_2O + 2HSO_4^- \rightarrow 2Ag^+ + 2SO_4^{--} + H_2O$

INTENSIFIERS

Intensification, as illustrated in Figure 151, is considered (1) proportional, if the density increase is directly proportional to the original density, (2) superproportional, if the percentage gain of density increases with increased original density, or (3) subproportional, if the percentage increase of density diminishes with increased density.

Proportional intensification is the most general and useful type, and this type of action is fulfilled or approached by most intensifiers. Superproportional intensification results from solvent or other inhibiting action which tends to prevent increase in the lower densities; while subproportional intensification results from partial failure to intensify in the intermediate and higher densities. Subproportional intensification is obtained with the chromium intensifier (*a*) when bleaching or redevelopment is incomplete, or (*b*) if stain (pyro developed) images are intensified under conditions which remove much of the stain.

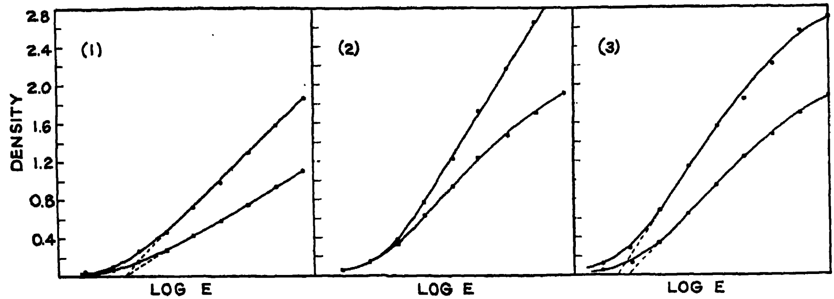

Fig. 151. Intensification: 1, proportional; 2, superproportional; 3, subproportional.

Well-known examples of intensifiers may be classified as follows:[1b,3]

1. Proportional Intensifiers
    - Chromium intensifier (bichromate-hydrochloric acid bleach; metol-hydroquinone redeveloper)
    - Mercuric chloride-bromide bleach; silver-potassium cyanide redeveloper (Monckhoven's)
    - Silver intensifier
2. Superproportional Intensifiers
    - Monckhoven's intensifier with slight excess of potassium cyanide in the redeveloping solution. Mercuric bromide bleach; sodium sulfite redeveloper
3. Subproportional Intensifiers[18]
    - Uranium intensifier
    - Chromium intensifier with incomplete bleaching or redevelopment

Ferricyanide-bromide bleach in combination with staining redeveloper and incomplete bleaching or redevelopment*

Mercuric iodide followed by a *p*-aminophenol redeveloper.

Action of intensifier solutions. Chemical intensification may be brought about by adding to the silver image, by partially or entirely replacing it by an optically denser material, or by altering the photometric constant. If an image is bleached in a dilute solution of potassium bichromate acidified with hydrochloric acid, and redeveloped in a nonstaining developer, a moderate increase in density will follow. It is still doubtful whether the chromium compounds are added to the silver or whether the double conversion merely increases the porosity and covering power of the grain; *i.e.*, alters the photometric constant. It is probable that some reduced chromium compound is present, since increase in the acidity of the bleach decreases the intensification. Strong acid, such as sulfuric, removes the intensification.[16]

The great majority of intensifiers increase the mass of the deposit. They may be subdivided into so-called *physical* and *chemical* types, according to their mode of action. The physical intensifiers deposit metallic silver or mercury on the developed silver grains. They obtain the energy for reduction from a reducing agent in the solution, the silver grains acting as nuclei for this reaction. A suitable solution can be made from silver nitrate, pyrogallol, and citric acid; or a mercury salt, metol, and citric acid.

Alkaline physical intensifiers are known, and a number devised by various workers are given by Wall.[20] A relatively stable alkaline physical intensifier containing silver nitrate, sodium sulfite, sodium thiosulfate, and metol, given by Crabtree and Muehler, gives proportional intensification and a neutral image. This type of intensification has the advantage of being permanent.

The typical chemical intensifier involves the dual process of bleaching and darkening. The bleach contains a soluble, oxidized salt which yields an insoluble silver compound and an insoluble, reduced salt. A well-known bleach is the soluble mercuric chloride, which attacks metallic silver and forms a mixture of silver chloride and mercurous chloride. Each grain is augmented by a quantity of mercurous chloride. Darkening can then be effected by any solution which renders the silver and mercurous chloride opaque, such as a developer, sodium sulfite, or ammonia. Experimentally, even saturated potassium bromide solution effects a darkening. With ammonia, the reaction darkens only the mercury salt to $Hg_2Cl \cdot NH_2$, which, in reality, is a dispersion of colloidal mercury in the "infusible white precipitate" of the ancient alchemists: $Cl—Hg—NH_2 + Hg$. Mercury-intensified images are not permanent unless they are completely reduced to mercury and silver or converted to sulfides.

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* Using the method of Wilsey,[19] but bleaching or redeveloping incompletely.

Mercury intensifiers. Mercurial intensification was studied by Chapman Jones,[21] who laid great stress on the necessity for converting the image to metallic mercury and silver if it is to be permanent. Since organic developing agents require sulfite in the solutions and this reacts with the mercurous chloride so that half the mercury passes into solution, he recommends that the image be treated with a ferrous oxalate developer after bleaching with mercuric chloride. This reduces the silver chloride and mercurous chloride quantitatively to the metals. The image may be intensified a second time by exactly the same method, for mercuric chloride acts upon metallic mercury exactly as it does upon metallic silver—

$$AgHg + 2\,HgCl_2 \rightarrow AgHg_3Cl_4,$$

and from this product ferrous oxalate removes the whole of the chlorine, as before. By repeated applications, therefore, the images produced have the following composition:

Original	*Intensified*			
	Once	Twice	Three times	
Ag	AgHg	$AgHg_3$	$AgHg_7$,	and so on.

This method of intensification was applied by Chapman Jones to the enlargement of particles of fine-grained silver, so that their size could be determined microscopically (p. 567).

Single-solution mercury intensifiers which give impermanent brownish-black images are known in many variations. They generally contain mercuric chloride as the oxidizing agent and an optimum quantity of potassium iodide or this combination and sodium thiosulfate[22] or sodium sulfite.[23] The soluble iodide may also be replaced by alkali thiocyanate,[24] in which case the thiosulfate or sulfite is usually omitted. The images obtained with the single-solution mercury intensifiers are useful but not permanent unless subsequently treated with a developer or dilute sodium sulfide.

The ferricyanides of the heavy metals oxidize the silver to silver ferrocyanide and are themselves reduced to insoluble ferrocyanides. The lead salt reacts thus:

$$4\,Ag + 2\,Pb_3[Fe(CN)_6]_2 \rightarrow Ag_4Fe(CN)_6 + 3\,Pb_2Fe(CN)_6$$

and produces a dense deposit, which may be further darkened by conversion of the ferrocyanides to sulfides.

The uranium intensifier is really a toning solution which contains potassium ferricyanide, uranyl nitrate, and oxalic acid. It is useful in cases of extreme underexposure since the degree of photographic intensification for low densities is of the order of 300 per cent.[18] The image is not permanent, being soluble in alkali.

Optical Intensification

If a silver image is bleached in oxidizing solutions containing halogen, such, for instance, as ferric bromide, and the resultant silver bromide is darkened to silver sulfide, the silver sulfide appears less dense than the original image; yet photographically its opacity is increased because its color has been changed to brown, which absorbs the blue light, to which the printing medium is sensitive. Such a procedure is known as *optical intensification* since it depends on the *color* of the transmitted light rather than on its *intensity*.

All processes of intensification and reduction could be included under this heading, because the image seldom undergoes a transformation without alteration of the ratio between its visual and photographic densities. Nevertheless, the heading is applied generally to processes involving change of color rather than mass. When a metallic silver deposit is converted to the brown sulfide, red chromate, or buff ferricyanide, although it appears to lose density, it shows greater contrast in printing. Wilsey,[19] following the suggestion of L. A. Jones, proved the usefulness, as an intensifier, of the stain produced by pyrogallol during development. If a negative is bleached in ferricyanide and bromide and redeveloped in pyrogallol, although the image appears to have lost a little depth, it will yield a stronger print. The increase in printing strength is directly proportional to the amount of stain and, hence, inversely to the quantity of sulfite in the developer. Table LX from Wilsey's paper gives the ratio of

TABLE LX

Redevelopment	*Original Development Metol-Hydroquinone, Permanganate Bleach*	*Original Development Metol-Hydroquinone, Ferricyanide Bleach*	*Original Development Pyro 5–10–10 Permanganate Bleach*	*Original Development Pyro 5–10–10 Ferricyanide Bleach*
	$\frac{\gamma_{ip}}{\gamma_{op}}$	$\frac{\gamma_{ip}}{\gamma_{op}}$	$\frac{\gamma_{ip}}{\gamma_{op}}$	$\frac{\gamma_{ip}}{\gamma_{op}}$
Pyro 5–10–0	2.00	1.70	1.15	1.80
Pyro 5–10–5	1.50	1.35	.95	1.40
Pyro 5–10–10	1.15	1.15	.80	1.15
Pyro 5–10–25	.95	1.00	.65	.95
Metol-hydroquinone	.80	.95	.55	.85

the γ of the intensified plate (γ_{ip}) to that of the original (γ_{op}) measured photographically on motion-picture film, as described later. The figures following the word "pyro" in the first column refer to the relative quantities of pyrogallol, carbonate, and sulfite expressed in grams per liter of solution. The permanganate bleaching bath removes any stain caused by the first development, while the ferricyanide leaves it to reinforce the stain produced in the second development. It is interesting to note that the effect of successive bleachings in ferricyanide and redevelopment in pyrogallol is cumulative (Table LXI).

TABLE LXI

Successive Bleaching and Redevelopment	*Original Development Metol-Hydroquinone Ferricyanide Bleach*	*Original Development Pyro 5-10-10 Ferricyanide Bleach*
Pyro 5–10–0	$\frac{\gamma_{ip}}{\gamma_{op}}$	$\frac{\gamma_{ip}}{\gamma_{op}}$
Once	1.70	1.80
Twice	2.10	2.20
Three times	2.40	2.45
Four times	2.65	2.70
Five times	2.80	2.85

Hickman and Weyerts[25] showed that silver sulfide is sensitive to light and accumulates metallic silver if illuminated under solutions containing free silver ions. Solutions of silver-sodium-nitrite and silver-sodium-sulfite, containing about 5 grams per liter of silver nitrate, are most effective.

Silver images converted to sulfide can be intensified in light (of all wave lengths from ultraviolet to 1.4 μ) under the solutions mentioned. The process, which readily permits very high intensification, has also been termed *optical intensification.*

The reaction in nitrite is shown to be a simple oxidation-reduction process which causes the metallic silver to deposit on the silver sulfide. The reaction in sulfite may be of a similar nature, but it also may take place through the medium of adsorbed poly-sulfur-bodies, in which case the generation of a diffusible reducing material is thought to precede the deposition of silver.

Color Coefficients

The relation of printing density to visual density is of importance (Chapter XVII, p. 645). One of the first to give such data for intensified images was Clerc,[26] who used Desalme's copper-tin intensifier. Nietz and Huse made a study of the relation between the original visual and photographic γ's and similar γ's after intensification.[18] To determine the actual printing density or printing γ in practice, it is necessary to print the negative on a material having a known characteristic curve, to develop it under standard conditions, and to calculate from the densities in the reproduction the amount of photographic light transmitted by each step of the original. Nietz and Huse and Wilsey worked according to the scheme pictured in three steps in Figure 152. In Section A, the visual densities of a sensitometric strip are plotted against log E in the usual manner. This is curve O_v, or the visual density of the original strip. After intensification, a new curve, i_v, or the visual densities of the intensified image, is obtained. As both the original and intensified silver deposits are likely to be colored, however, the printing densities are different from the visual, giving curves O_p and i_p, where the subscript p = printing density. These printing density curves are, of course, only found as the result of the graphical analysis, but they are printed in the first quadrant for the sake of clarity. The original and intensified strips, corresponding with O_v and i_v, are printed onto a standard mate-

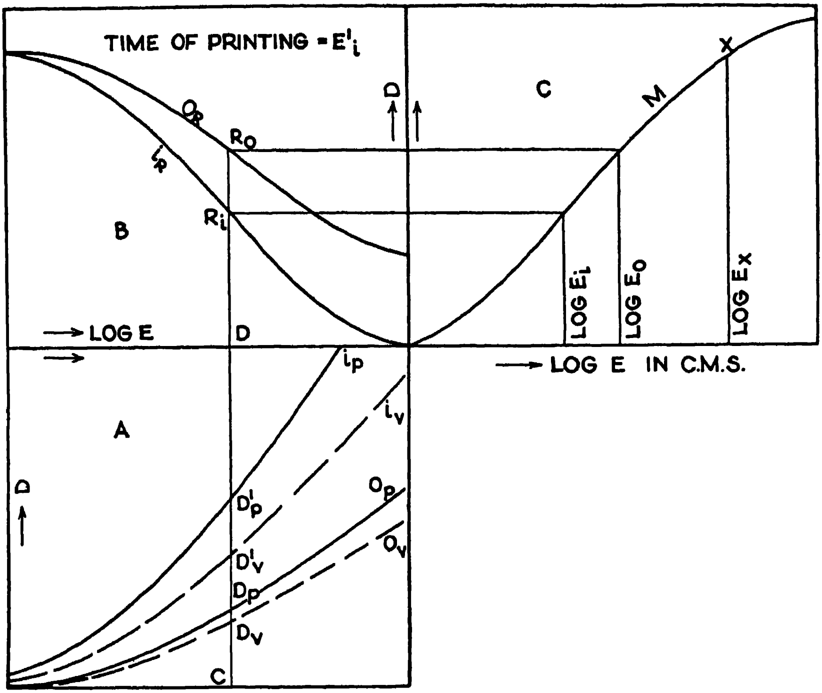

FIG. 152. Scheme for determination of the relation between visual and photographic γ's before and after intensification.

rial, such as motion-picture positive film, and yield the composite curves O_r (original, reproduced) and i_r (intensified, reproduced) in the left-hand upper quadrant. They represent the summation of the original and intensified *photographic* γ curves plus the natural γ of the printing material. By projection from any points on O_r or i_r to M, the natural γ of the positive film shown in the third quadrant, the actual photographic, *i.e.*, printing exposure transmitted by the original materials can be calculated from readings along the A axis.

Having determined the printing density, D'_p, of the intensified image, the selectivity coefficient for the given density is given by the ratio D'_p/D'_v. Thus, the photographic density relative to the visual density D_v is evaluated for a particular density. The ratio of the slopes at the points D'_p and D'_v is defined as the *selectivity gradient coefficient;* that is,

$$\frac{\dfrac{dD'_p}{d\log E}}{\dfrac{dD'_v}{d\log E}}.$$

If the value of the selectivity gradient coefficient is constant over a range of values of log E, the image may be considered to have a color coefficient. If the photographic and visual density-log E curves have sufficient straight line to determine γ, the color coefficient will be the ratio of the photographic and the visual γ's. The color coefficients of a number of intensifiers determined by Nietz and Huse varied from 1.0 for chromium redeveloped with amidol and mercuric chloride redeveloped with amidol to the high value of 2.52 for the brownish colored uranium intensification. Similarly, Crabtree and Muehler[1b] determined the color coefficients of selected intensifiers (chromium, mercury, and silver) and reducers suitable for motion-picture work.

MISCELLANEOUS METHODS OF INTENSIFICATION AND REDUCTION

In this treatise, it is impossible to include more than a brief consideration of several miscellaneous methods of intensification and reduction and their effects. The voluminous literature on the subject and the varied and involved processes are well presented in many sources.[19,1b,27]

1. *Harmonizing* is the term usually applied to a process combining the advantages of both intensification and reduction. The method attributed to Eder[10] consists of bleaching with bichromate, hydrochloric acid, and potassium bromide, followed by partial redevelopment and the fixing out of the remaining undeveloped silver halide. The low densities of the image, which redevelop to completion, tend to be intensified, while the higher densities, which are progressively less completely developed, are reduced superproportionally. Thus, the method is useful for lowering the contrast of underexposed-overdeveloped images. A modified bleach given by Piper,[9] which contains only

potassium ferricyanide and potassium bromide, effects reduction only if a nonstaining developer is used.

2. Photographic intensification or reduction can be effected by converting the silver image to an image of different spectral absorption. Such processes include metal ferricyanide toning methods, which convert the image to ferric, cupric, or uranyl ferrocyanides. These metallic ferrocyanide images may then be dye toned or converted to colored organic salts such as nickel dimethylglyoxime. Also, the silver image may be converted to halide and then redeveloped in a coupler developer.

3. The reduction of photographic densities by excessive treatment in fixing baths is well known,[28] and early references to (1) the use of alum baths after fixing for reducing density[29] and (2) the reducing action of highly acidified sulfite-thiosulfate solutions[30] can now be attributed to the ability of sodium thiosulfate to dissolve silver provided a suitable oxidizing agent is present (Chapter XIII, p. 515).

The type of reduction given by highly acidified fixing solutions is described by Crabtree and Russell[28c] as essentially proportional for high-speed negative film but between subtractive and proportional for motion-picture positive film. The rate of reduction is greater for positive than for negative film and increases in such solutions with (1) a decrease in grain size of the silver image, (2) a decrease in pH from 4.0, (3) increased bisulfite concentration at pH 3.0, (4) increased thiosulfate concentration, to a maximum at 30 per cent, and (5) the addition of ammonium chloride, potassium bromide, or potassium iodide. The rate of reduction was decreased by (1) exhaustion or addition of silver halide, (2) addition of sodium sulfate.

4. Intensification or reduction of a negative can be most safely effected by making a duplicate through the use of (1) the usual process involving the making of (*a*) a master positive and (*b*) a duplicate negative,[31] (2) the reversal process of developing, bleaching, resensitizing, exposing, and developing, or (3) the direct developing type of materials, solarization being depended upon to produce reversal. With such duplicates, increase or decrease in contrast of the original image is possible over a wide range by a variation of the development.

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CHAPTER XV

TONING

THE COLOR OF SILVER DEPOSITS

The silver image produced by development is normally black or gray. This is also true of precipitated silver produced by reduction. According to Lüppo-Cramer,[1] who confirmed and extended work by Liesegang, when silver nitrate in aqueous solution is reduced by pyrogallol and alkali (sodium carbonate), black, finely divided silver (the A form) is obtained, whereas pyrogallol alone gives a grayish-white coarse-grained precipitate (the B form). The A form is obtained with all alkaline developers and is likely to be colored by the adsorption of oxidation products of the developer; the B form results if ferrous sulfate, quinol, or metol is used in the absence of alkali. If sulfite is present in the developer, the silver formed tends to be intermediate between the A and B forms.

Lüppo-Cramer suggested that the particular form of silver obtained depended upon the rate at which the silver compound was reduced; a low rate of reduction gives time for ripening to take place and produces the B form. In later investigations, however, Lüppo-Cramer[2] was able to reduce a precipitate of silver citrate very slowly to deep black silver, which upon boiling with water became light gray in color. The influence of citric acid in this reaction is specific since it is independent of the reducing agent, and most of the other acids do not give the same effect. For example, if silver nitrate is reduced by metol in the presence of citric acid, a black, dispersed silver is obtained, which settles only very slowly, whereas, with nitric or phosphoric acid in place of citric acid, gray-white silver is obtained as glistening particles.[3] Pyrogallol and ferrous sulfate give results similar to metol except that, in the former case, the oxidation products of the pyrogallol tend to act as a protective colloid. Tartaric acid behaves similarly to citric acid, but oxalic acid gives an intermediate product.

Eder[4] shows by a number of instances that similar results are obtained in wet collodion; for example, the addition of acids such as nitric, sulfuric, and phosphoric gives a whiter silver, whereas acetic acid gives a brown, and citric acid a black deposit. In the formulas for intensifying wet plates, citric acid was generally used. It may also be mentioned that the addition of sodium acetate gives black silver in the reduction of silver nitrate by ferrous sulfate or quinol in aqueous solution.

Lüppo-Cramer found that microscopical comparison of the two forms most different in color, namely, those obtained in gelatin solution with and without the addition of citrate, showed no characteristic differences in either shape or size; in both cases, the particles were much smaller than those obtained in the presence of phosphoric acid. Nevertheless, there was a difference in the internal structure of the separate particles, since the black silver obtained with the addition of citrate was much more quickly bleached by mercuric chloride than the grayish-white silver formed in the absence of citrate. This differentiation of the internal degree of dispersity of particles determined by means of mercuric chloride, when microscopic observation fails to show any difference, has often been used by Lüppo-Cramer: For example, he calls attention [5] to the fact that the silver produced in a negative by chemical development is generally said to be more granular than that obtained by physical development but points out that this can only be true of the external appearance since the rapid attack of mercuric chloride shows that it is much more highly dispersed. Liesegang [6] and Kohlschütter [7] call attention to the fact that black silver has a much higher degree of dispersity than gray silver. In Carey Lea's historic researches on the allotropic forms of silver, various references may be found to phenomena which have been explained on the assumption of a high internal dispersity of the various forms, this dispersity being maintained by a sheath of colloidal silver salt around the particles forming any particular aggregate.

Results obtained in a systematic investigation with the electron microscope in the Kodak Research Laboratories show that both gray and black silver prepared according to Lüppo-Cramer's instructions consists of crystals of triangular or hexagonal outline (111 octahedral faces); but, whereas the gray silver crystals are large (up to 100 μ) and untwinned, the black ones are very small (up to 0.1 μ) and are present in clusters. This shows that the difference in color is due to a difference in size of the crystals, which is confirmed by the fact that the two forms give the same crystal lattice diagram with X-rays.

As is shown elsewhere (Chapter VIII, p. 311 and Chapter XXI, p. 834), the silver of the developed image is filamentary in form and quite different from the silver crystals produced by reduction from solution. Nevertheless, both black and gray forms of silver occur in photographic work. For example, the addition of soluble bromides to a developer to reduce the effect of overexposure has a considerable influence on the character of the reduced silver. If large quantities of bromide are present, the velocity of development is greatly reduced and, instead of the ordinary black silver, a light gray form is produced.[8] This gray silver is due to the orientation of the minute plates, which lie more or less in a plane and so reflect light specularly. After fixation, the gray silver is much more readily attacked by persulfate than the black silver, since the latter, owing to its higher dispersity, contains adsorbed matter in greater quantity and the attack of the persulfate is thereby retarded.[9]

For the production of direct positives to be viewed by reflection, as in the ferrotype process, the silver in the highlights should be more or less white. From the discussion above, it is obvious that such a result is best produced with collodion owing to its lesser protecting action, especially if a silver solvent is added to the developer.[10] The positive effect produced when a negative is viewed by reflected light against a dark background is due to the different types of silver formed in the highlights, middle tones, and shadows. That the silver differs is shown by the fact that in mercuric chloride solution the shadows begin to bleach first, then the middle tones, and, finally, the highlights.

While the silver produced by normal development is black or gray, silver images may be obtained having bright colors if the particles of silver are small in comparison with the wave length of light. This can be accomplished by restrained development with solutions containing silver solvents, and the use of such developers with emulsions of fine grain is common for the production of lantern slides. These colored images are directly analogous to the colored sols of colloidal silver which have been investigated extensively by Lüppo-Cramer.[11] He used a nucleus sol of silver made according to Carey Lea's well-known dextrin method, which he found to give the best results if prepared as follows:[12]

> To a solution containing 20 grams of commercial dextrin and 20 grams of pure sodium hydroxide in 500 cc. of water are added 15 grams of silver nitrate dissolved in 100 cc. of water. There is rapidly formed a deep reddish-brown solution, to which, after 20 minutes, are added 500 cc. of 96 per cent alcohol. After a further 15 minutes, the supernatant cloudy liquid is decanted off; the residue then dissolves readily in water, a 5 per cent sol being easily obtainable.

In the first experiments which Lüppo-Cramer describes[13] for making colored silver sols, he used a gelatin washed ten times to get rid of all traces of chlorides. One hundred cc. of a 10 per cent solution of this gelatin are diluted with 400 cc. of water, and 20 cc. of a 10 per cent solution of silver nitrate are added, the temperature being 25° C.; actinic light is excluded. To separate 100-cc. portions of this solution are added the following quantities of a 0.05 per cent colloidal silver solution made by diluting the stock solution prepared in the manner described above: (*a*) 0 cc., (*b*) 0.5 cc., (*c*) 2 cc., (*d*) 5 cc., (*e*) 10 cc. Each solution is then reduced by the addition of 4 cc. of a 10 per cent alcoholic solution of quinol. If the transmission colors are compared after 30 minutes, the solutions first being diluted, they are found to be (*a*) blue green, (*b*) pure blue, (*c*) bluish violet, (*d*) ruby red, (*e*) yellowish brown. The colors can be seen best, however, by diluting the sols with an equal volume of 10 per cent gelatin solution and then coating on glass. When the films dry, the yellow changes to red, and the red to blue, but the colors are regained on moistening.

Instead of using the silver sol as a nucleus, the silver nitrate-gelatin mixture may be exposed to light for some time before the reducing solution is added. This gives rise to silver nuclei, the reaction being comparable with that discovered by Svedberg, who showed that ultraviolet light forms gold nuclei in solutions of gold salts exposed to its action.[14] Similar colors are obtained if silver bromide is used in place of silver nitrate,[15] but the phenomenon is made more complex by the adsorption colors produced from the oxidation products of the developer.

Any of these methods will produce a range of colors by the systematic variation of one of the components of the developer if this component can react with the silver compound. Thus, a color scale may conveniently be formed by additions of varying quantities of potassium citrate to the same quantity of the reduction mixture, as follows: To 500 cc. of a 2 per cent solution of gelatin are added 50 cc. of the nucleus silver sol and 20 cc. of 10 per cent silver nitrate solution, the temperature being 35° C. To portions of 100 cc. are then added (*a*) 0 cc., (*b*) 1 cc., (*c*) 4 cc., (*d*) 10 cc., of a one per cent solution of potassium citrate, followed by 4 cc. of a 10 per cent alcoholic solution of quinol. After 20–30 minutes, the colors are: (*a*) yellow green, (*b*) yellow red, (*c*) red, (*d*) blue violet. Intermediate colors can be obtained by varying the quantities of potassium citrate (*e.g.*, 0.5 cc. gave a ruby red after drying), but an increase to 20 cc. shows no further effect. It is seen that there is a high concentration of nucleus sol (10 cc.) in each experiment and that the effect of increasing the amount of potassium citrate is to change the color towards the blue end.

These experiments show that with the same concentration of silver nuclei and the same quantity of silver nitrate solution reduced, all the colors can be obtained by the addition of varying quantities of citrate. In the first experiments described, the different colors were obtained by using varying quantities of silver nuclei for the same quantity of silver nitrate solution, the reason for this method being that the nuclei would grow directly by deposition on them of fresh silver as it was formed by the reducing process; thus, the smaller the number of nuclei originally present, the greater the size to which they would grow and the greater the displacement of the transmission color toward the blue.

The relation between the size of the particles and the color of actual silver images formed on lantern plates was studied by Chapman Jones.[16] Applying Rayleigh's theory of the diffraction of light by electrical conductors of small size to the experimental results which Zsigmondy achieved with the ultramicroscope in gold sols,[17] Mie[18] had established the dependence of color on size in metal sols. This dependence included the influence of the specific absorption of the metal, since the particles could not be considered ideal conductors. Zsigmondy himself interpreted his experimental results by connecting the color with the distances between the particles rather than with their size. Chapman Jones, however, considers that the distance may have only an indirect influence. His method of investigation was to enlarge the particles by depositing mercury upon them (see page 552). The enlargement can be performed in definite steps and was continued until the particles were of measurable size. In a later note, Chapman Jones corrects his measurements for an optical effect produced in the microscope; his corrected figures show that the light is scattered by particles of a diameter equal to half the wave length of the scattered light, which is in complete agreement with the theoretical conclusions previously advanced and gives a satisfactory explanation of the color of the silver deposits.

It must be remembered that the wave length of light considered is that in gelatin, which is approximately two thirds of the wave length in air. The mean wave length of the scattered light enters the visible spectrum for particles of 0.13 μ, and particles of this size become increasingly yellow as their size increases, until at 0.16 μ the color is orange and tends to become pink, and at 0.20 μ, the deposit is reddish brown. As the particles grow in size, the saturation of the color of the image diminishes and the image becomes brown and then gray. Some very peculiar colors, which have not been investigated specifically in relation to the size of the particles, are formed by the use of small quantities of thiocarbamide in a developer containing bromide, the images being produced on fine-grain plates. These images are bluish, ranging through lilacs to pinks and purples. There is little doubt that with the aid of the electron microscope a systematic investigation of the color of such images would show that all the phenomena observed can be explained on the basis of the scattering of light by small particles.

While use has been made of the color of images composed of finely divided silver to produce very beautiful lantern slides, the same effect is frequently undesirable in that fine-grain emulsions of the types used for printing give brownish or olive-green tones, which are less satisfactory than the black silver obtained with coarser deposits. A change in the color of such fine-grain silver deposits can be obtained by additions to the developer, the compounds used for this purpose being known as *blue-black addition agents.*

It is convenient to classify the compounds capable of giving a blue-black tone into three groups: The first includes heterocyclic bases capable of co-ordinating with silver bromide, such as chlorbenzotriazole,[19] quinoline and its derivatives,[20] quinine,[21] and numerous similar compounds.[22] The second group includes iodonium salts, such as diphenyl iodonium nitrate.[23] The third group includes many organic sulfur compounds, such as rhodamine and *N*-substituted rhodamines, and pseudothiohydantoin.[24] One theory of the action of these compounds is that they are adsorbed to the silver halide and so diminish the solvent action of sodium sulfite in the developer, and this is possibly the action of the first two groups in the above classification.

Jelley* found a cause of brownish tones, distinct from the degree of dispersion of the silver granules comprising the image: Some of the light passing through the photographic image is reflected many times from minute facets on the silver grain, and at each reflection the light becomes yellower on account of the surface color of silver. Furthermore, the reflected light may traverse a considerable distance in the emulsion before making its escape. It follows, then, that reducing the reflecting power of silver should make the image less brown. This is the case; dilute solutions of an alkali polysulfide, hypo-alum toning baths, and alkaline thiourea make the image much colder in tone, even though the time of treatment is so short that only a low percentage of the silver is converted to silver sulfide. A very brief treatment with a gold-toning solution turns the image black, and the formation of a thin film of silver bromide on the granules followed by the adsorption of a red, blue, green, or violet dye makes the image colder in color. Jelley also noted that the blue-black images produced by developers containing the organic sulfur compounds of group 3 contain an appreciable quantity of silver sulfide and have a lower reflecting power if examined microscopically by vertical illumination.

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* E. E. Jelley, unpublished work.

CHEMICAL TONING

The modification of the color of a silver image by a change in its chemical composition is the object of the operation known as *toning.* To understand the historical development of this subject, it is necessary to resume the history of the processes by which paper prints have been produced. The earliest printing papers were made by treating a paper surface with solutions alternately of sodium chloride and silver nitrate, so that a layer of silver chloride with an excess of silver nitrate adsorbed to it was produced on the paper. When printed from a negative, the exposure being a number of minutes to skylight, the silver halide is converted into photo-silver. This photo-silver, studied so completely by Carey Lea,[25] is a complex of metallic silver and some silver chloride which is protected by the metallic silver and so resists the action of the thiosulfate bath used to remove the excess of silver chloride and thus fix the image. An improvement in this paper was effected in 1850 by Blanquart-Evrard, who used albumin as a vehicle for the silver chloride. The paper was coated with albumin containing dissolved chlorides and was then floated face down on a bath of silver nitrate to produce the silver chloride and sensitize the layer. In addition to the silver chloride, the albumin paper contained silver citrate produced by the addition of citrates to the albumin coating solution. This paper was used for many years as a printing paper and was displaced only when collodion and gelatin emulsions of silver chloride and silver citrate were prepared.

In these processes in which the image was formed by prolonged exposure to light, an excess of silver nitrate was necessary to produce sensitivity, and the image which remained after fixing was weak and unpleasant in color; in addition, it was unstable and easily attacked by the atmosphere and, to some extent, by light. This was remedied by the deposition of metallic gold upon the image. Gold had been used for a similar purpose in the daguerreotype process. Before fixing, the paper carrying the printed image was immersed in a solution of gold chloride containing a compound such as borax or sulfocyanide,* and the gold was deposited upon the silver image, strengthening it and changing its color to a purple and, finally, to a deep bluish purple, almost a black. After fixing, to remove the unchanged silver halide, an image of a pleasing purplish color was obtained, a considerable part of which consisted of metallic gold and was therefore stable. For details of the reactions involved in these methods of toning, reference should be made to the abundant literature.[26]

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* These compounds form complex ions with the gold and thus stabilize the solution against precipitation by the proteins of the gelatin.

The process of toning with gold persisted until the printed-out images composed of photohalide were replaced by developed silver images, when the earlier silver chloride papers containing free silver nitrate were displaced by silver chloride emulsions which could be developed in alkaline developers. The image of these papers is of a pleasing black, almost blue black, although by restrained development, especially in the presence of solvents, brownish images are obtainable.

To modify the color of developed images, three methods are in general use: (1) The silver image may be converted into silver sulfide or its analogues, silver selenide and silver telluride. These compounds have brown and purple colors, much warmer than that of the silver deposit, and such toning methods have a very great vogue. (2) The silver image may be replaced by means of a series of chemical reactions producing a compound of some other metal. (3) The image may be replaced, to some extent, by a dye which gives the image its characteristic color.

Sulfide Toning

Metallic silver readily combines with sulfur to yield silver sulfide, which is one of the least soluble and most stable of silver compounds. Silver images are easily converted to silver sulfide. The various methods of sulfide toning may be divided into two categories: direct methods, in which the silver image is converted by a single operation into silver sulfide; and indirect ones, in which the silver is first transformed into silver chloride or bromide, which is then acted upon by a solution of sodium sulfide to convert it to silver sulfide.

For direct methods of sulfide toning, either colloidal sulfur or a polysulfide may be used. The reaction between silver and sulfur is shown in an interesting, though impractical, manner by boiling a Velox print in water to which some flowers of sulfur has been added. Slow toning takes place. Sulfur in a molecular state of subdivision reacts at lower temperatures; thus, it is possible to tone certain types of photographic paper by transferring the prints direct from the fixing solution to a 2–5 per cent solution of hydrochloric acid. The sodium thiosulfate is decomposed by the acid to form, among other products, colloidal sulfur, which remains in the gelatin when the prints are washed. The washed prints will tone to a rich brown if stored in a moist state for about twenty-four hours. The well-known "hypo-alum" toning bath works on this principle. In its earlier form, it consisted of a solution of sodium thiosulfate to which potassium alum had been added. This was heated to about 50° C., and the prints were allowed to remain in the solution until sulfiding was judged to be complete. In its present-day form the solution contains 10 to 20 per cent thiosulfate, about 3 per cent potassium alum, about 1 per cent each of silver nitrate and sodium chloride. The thiosulfate is dissolved in cool water and the alum in hot water. When the alum solution is added to the thiosulfate, colloidal sulfur is precipitated. Then the silver nitrate is dissolved in a small volume of water, the sodium chloride is added, and the solution containing the resulting precipitate of silver chloride is added slowly to the hypo-alum solution while stirring the latter solution rapidly.

Another direct method of sulfide toning depends on the action of alkali polysulfides. Solutions of sodium, potassium, and ammonium sulfides readily dissolve sulfur to form mixtures of di-, tri-, tetra-, and penta-sulfides. These solutions part with sulfur and rapidly convert a silver image to one of silver sulfide. Alkali polysulfide solutions have a strong softening action on gelatin, however, so that their popularity for toning is on the wane. Shaw[27] used a solution containing barium sulfide and sodium *m*-nitrobenzene sulfonate. This slowly decomposes, the *m*-nitrobenzene sulfonate being reduced. In the presence of finely divided silver, the reaction velocity is greatly increased and silver sulfide is formed. On many occasions, a toning technique has been suggested in which the silver prints are placed in a solution of sodium sulfide and are then transferred, without washing, to an oxidizing solution, such as ammonium persulfate or potassium ferricyanide. The sodium sulfide is rapidly oxidized, and the silver is very largely converted to silver sulfide.

Indirect methods depend on the conversion of the silver image to silver chloride or bromide by means of a bleaching bath and the subsequent conversion of the halide to silver sulfide in the sulfiding bath. Many different bleaching baths have been proposed, which, in general, contain an oxidizing agent and a soluble halide. Combinations of this type are potassium permanganate with hydrochloric acid, potassium dichromate with hydrochloric acid, potassium ferricyanide with potassium or ammonium bromide. Lumière and Seyewetz recommended the use of quinone and quinonesulfonic acids.[28] Mercuric and cupric salts have been used in bleaching baths in order to convert the silver of the image to a mixture of silver halide with a mercurous or cuprous halide. Of these various combinations, by far the most popular is the potassium ferricyanide-potassium bromide one. The action of this bleach may be written as

$$[\mathrm{Fe}(\overline{\mathrm{CN})_6}] + \mathrm{Ag} + \mathrm{Br}^- \rightarrow [\mathrm{Fe}(\overline{\mathrm{CN})_6}] + [\mathrm{Ag}^+\mathrm{Br}^-]\ \text{cryst.},$$

in which the silver gives up the electron required to reduce the ferricyanide ion to ferrocyanide.

The most usual sulfiding bath is a dilute solution of sodium sulfide. Other compounds which have been used include sodium orthothiostannate, sodium thioantimonate, sodium thiomolybdate, and alkali polysulfides. Sodium thioantimonate tones the image an orange shade of sepia because of the co-precipitation of antimony pentasulfide with the silver sulfide. Orthothiostannates give the same tone as sodium sulfide, as the stannic sulfide stays in solution to form a metathiostannate. Polysulfides, particularly pentasulfides, deposit sulfur with the silver sulfide and therefore give a yellow image. Tripel[29] proposed the use of organic sulfur compounds in strongly alkaline solutions. These solutions have the particular merit of being odorless even when greatly diluted, whereas other sulfiding agents give some hydrogen sulfide on dilution. One such odorless sulfiding solution contains 0.1 per cent thiourea and 0.4 per cent sodium hydroxide. Its reaction with silver bromide is

$$\begin{aligned}2\,\mathrm{AgBr} + (\mathrm{NH_2})_2\mathrm{CS} + 2\,\mathrm{NaOH}&\\ = \mathrm{Ag_2S} + (\mathrm{NH_2})_2\mathrm{CO} + 2\,\mathrm{NaBr} + \mathrm{H_2O}.&\end{aligned}$$

It is essential that caustic alkali be used; otherwise, the rate of solvent action of the thiourea on the silver bromide becomes an important factor, and yellowish tones are produced. For a similar reason, the concentration of thiourea must not exceed 0.1 per cent.

The silver sulfide image may be any color from purplish brown to brownish yellow. Methods of controlling the color have been described in photographic literature ever since 1900, when Robins [30] published a series of papers on sepia toning. An excellent survey of the subject is given in a translation of a number of papers by Wiegleb.[31] Hickman [32] recognized that the silver sulfide particles should be kept as compact as possible to avoid yellowish-brown tones and proved his contention by bleaching slightly dampened prints with chlorine or bromine gas. This kept the silver halide as compact as possible, and good tones were then obtained on sulfiding. On the basis of an extended microscopical study of silver sulfide images, Jelley [33] came to the conclusion that their color depends on the nature of aggregation of the silver sulfide molecules. Thus, an image consisting of particles 2 μ in diameter is gray by transmitted light; one which is highly dispersed is brownish yellow. Mixtures of various sizes of grains with various proportions of colloidally dispersed silver sulfide produce the whole range of good and bad sepias. The indirect process which uses ferricyanide tends to change some of the silver to colloidal silver sulfide, there being three main ways in which this happens:

1. Insufficient development of the print gives a somewhat dispersed silver image which is further dispersed upon toning.
2. Traces of thiosulfate left in the prints by inadequate washing cause silver bromide to go into solution during the bleaching stage, and subsequent sulfiding produces yellowish tones.
3. Sodium sulfide solutions are oxidized by the air to yield sodium thiosulfate. If ferricyanide is left in the prints as a result of an inadequate washing before they are transferred to the sulfiding bath, the sulfide diffusing into the emulsion is destroyed by the ferricyanide and leaves the thiosulfate free to attack the silver bromide. By the time the ferricyanide is reduced and the sulfide is able to do its work, the silver thio-

sulfate complex has diffused considerably and forms colloidal silver sulfide. To expedite the removal of ferricyanide ions from the prints, Jelley recommends making the emulsion alkaline. This is achieved by adding sodium carbonate to the ferricyanide bleach. Previously, Bullock [34] had noted that less yellow tones were obtained if the prints were passed through a sodium carbonate solution between bleaching and sulfiding.

The formation of colloidal silver sulfide during indirect toning is greatly reduced by immersion of the prints in a solution of sodium sulfide or alkaline thiourea *before* they are bleached. During the bleaching operation, some silver sulfide is formed, which apparently prevents the dispersion of the bulk of the silver sulfide produced in the sulfiding bath in the usual manner. By the direct processes, particularly hypo-alum toning, a massive deposit of silver sulfide is formed which is much more purple than the tones obtainable by the indirect processes; and they are consequently preferred for chloride and chlorobromide papers. The indirect processes are best for fast bromide papers, which tend to give too cold a tone.

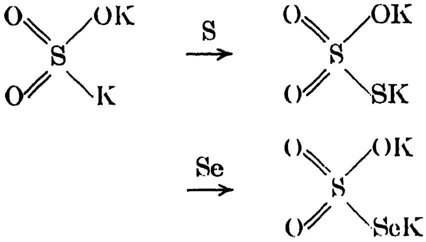
Selenium and Tellurium Toning

As might be expected, selenium and tellurium, occurring as they do in the same group and subgroup of elements as sulfur, form equally stable compounds with silver. Silver selenide and telluride, Ag_2Se and Ag_2Te, are permanent, dark-brown pigments eminently suitable as substitutes for the plain silver image. Tellurium was probably the first to be suggested as a toner, for, prior to a few remarks by Thorne Baker in 1901,[35] no mention of these elements occurs in photographic literature. Thorne Baker found that if a solution of tellurium tetrachloride produced by dissolving tellurium in aqua regia is diluted and applied to bromide prints, toning takes place according to the equation:

$$TeCl_4 + 6\ Ag \rightarrow Ag_2Te + 4\ AgCl.$$

The image, consisting chiefly of silver chloride, has to be sulfided or redeveloped to secure permanence.

There is this broad chemical difference between sulfur and its two group mates: that, whereas sulfur prefers a state of oxidation or combination, selenium and tellurium tend to separate in elementary form from slightly reducing solutions. Some methods of toning utilize this property; baths are compounded which precipitate the elements directly upon the image and form mixtures of silver and selenium or tellurium or simply silver selenide or telluride. In the patent of Rehländer,[36] finely divided selenium is boiled with sodium or potassium sulfite, sulfide, or thionates; it enters the molecule and produces compounds analogous to those which would be produced by boiling the same potassium salts with sulfur. Thus, as potassium sulfite adds sulfur to produce thiosulfate, so



selenium is taken up with the formation of the selenosulfate. When toning takes place in selenosulfate, the selenium is simply withdrawn according to the equation

$$Na_2SSeO_3 + 2\,Ag \rightarrow Ag_2Se + Na_2SO_3.$$

Buffered solutions of sodium selenite in sulfite solution, if used in the presence of thiosulfate, form excellent direct toning baths. Selenosulfate is believed to be the toning agent. The selenothionates are chain compounds and are produced from alkaline sulfides, probably by absorption of oxygen upon boiling. Rehländer's selenodithionate may be KO—S—Se—S—OK, analogous to potassium trithionate. Its toning power is similar to that of selenosulfate.

Tellurium is much more difficult to render soluble. Sulfite is practically without action, but sulfide dissolves it, especially if fused to form a sulfotellurite. The solution acts like the selenosulfate.

Toning with these metals has been completely surveyed by Kieser,[36] who gives extensive patent references. Bullock worked extensively on the practical use of these toners.[34]

The image may be bleached in ferricyanide and bromide and darkened in selenosulfate and ferrous oxalate, the latter being included to reduce the silver bromide. If the oxides of selenium and tellurium are dissolved in mineral acids, the solutions possess no toning powers unless they contain a second radical giving an insoluble silver salt. Thus, solutions of selenium dioxide or tellurium monoxide in sulfuric or phosphoric acids yield no selenide or telluride unless thiocyanate or bromide is present. The action is then

$$(\mathrm{TeO\ H_2SO_4}) + 4\mathrm{Ag} + 2\,\mathrm{KSCN} \rightarrow \mathrm{Ag_2Te} + 2\,\mathrm{AgSCN} + \mathrm{K_2SO_4} + \mathrm{H_2O},$$

where the acid is shown separately from the metallic oxide to denote that the tellurium is in solution in excess acid rather than as a definite sulfate. Whatever the reaction, the final toned print has a deep brown color, colder and less yellow than that of silver sulfide. The image may be rendered permanent by treatment with soluble sulfide, which converts any silver compound to sulfide. Theoretically, silver selenide is the most permanent of the three compounds because it is the least soluble, but Bullock showed that prints treated with an additional sulfiding bath are the most permanent to bright sunlight.

The simple colored salts of silver suffer from lack of stability and too easy solubility in dilute acids to be useful for toning purposes. The silver image placed in alkaline chromate solution does not bleach unless an acid is added to combine with the alkali and the reduced chromic oxide. Under these circumstances, silver dichromate is formed, which is soluble, and the picture dissolves. The reddish silver arsenate may be formed from a slightly acidified solution containing arsenic pentoxide, with or without an extra oxidizing agent. Similarly, the buff-colored silver phosphate may be formed from ferricyanide solutions containing phosphate.

Toning by Metallic Salts

The colored metallic salts which may be precipitated in gelatin by the agency of the silver image are legion. In general, a solution tones if it contains

(*a*) a radical yielding a soluble silver salt;
(*b*) an oxidizing agent enabling (*a*) to dissolve the image. The oxidizer itself becomes reduced to a compound which reacts with:
(*c*) a metal ion, producing a colored insoluble salt.

The most common oxidizing agent is potassium ferricyanide, which is reduced to potassium ferrocyanide. This may be combined with copper sulfate to produce red and brown tones, with iron citrate to give blue tones, or with uranyl nitrate to obtain other brown and red tones. Large quantities of citrates, acetates, and oxalates are sometimes added to buffer the solution and keep the highlights clean by colloidal protection; in fact, the published toning formulas show a multitude of variations. The essential toning action is the formation of an insoluble metallic ferrocyanide. The copper formula may be taken as a typical example:

$$4\,K_3Fe(CN)_6 + 2\,CuSO_4 + 4\,Ag \rightarrow 2\,Ag_2SO_4 + Cu_2Fe(CN)_6 + 3\,K_4Fe(CN)_6.$$

The two stages are best pictured in ionic notation, as follows:

$$Fe(\overline{CN)_6} + Ag \rightarrow Fe(\overline{\overline{CN)_6}} + Ag.$$

$$2\,Cu^{\cdot\cdot} + Fe(\overline{\overline{CN)_6}} \rightarrow Cu_2Fe(CN)_6.$$

There are other methods of toning in which the simple salt comprises the three functions (*a*), (*b*), and (*c*) enumerated above. The higher compounds of vanadium and molybdenum in contact with metallic silver reduce to the lower insoluble colored salts.[37] The colored salts of nickel and cobalt have also been pressed into use.[38]

Dye Toning

With the advance of color photography, notably in the motion-picture field, and the need for producing brightly colored images of definitely specified hues, the processes of dye toning have been used extensively.

As long ago as 1851, Persoz fixed an organic coloring matter by the chrome salts left when gelatin sensitized by bichromate is printed out under a negative. In 1892, Villain found that a little vanadate added to the bichromate bath hardens the gelatin and extends its ability to fix dyes. Such colors as alizarine red, galloflavine, and anthracene brown can be firmly fixed—not, as generally supposed, by retention in the gelatin owing to an altered physical condition but by absorption or combination with the chromic and vanadic residues. Richard[39] originated the modern method of dye toning when he showed that a developed silver image can be converted to an insoluble salt having a mordanting power or affinity for dyestuffs.

The first successful exponent of the art appears to have been Traube,[40] who patented [41] the well-known iodide process of dye toning. The silver is bleached in iodine or ferricyanide and iodide, washed, and immersed in a solution of basic dye for from ten minutes to twenty-four hours. The solution, which should contain about 0.1 per cent of dye, is preferably maintained slightly acid with acetic acid, partly because the gelatin is thus kept in a permeable condition and partly because a basic dye takes best in a slightly acid solution. A thorough washing removes mechanically retained dyes from the highlights and, with drying, completes the process. Typical dyes which adhere to the image but wash completely from the gelatin are rhodamine 6G; acridine orange; methylene, malachite, and brilliant greens; methylene blue; and crystal violet.

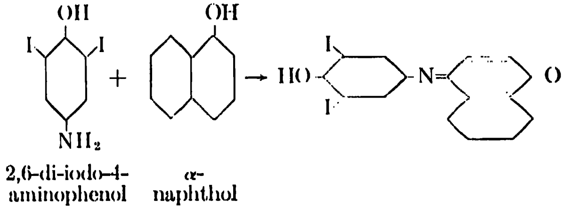
It was found in early work that appreciable quantities of dye were absorbed by silver iodide images only when they were contaminated with impurity. After a plain iodine bath, the impurity is iodide ion. In the language of Fajans and Frankenburger, the silver iodide is converted to the *iodide body*. The iodide body fixes the dye in one or both of the following ways: It peptizes the silver iodide, rendering it electrically charged and of enormous surface, affording both the opportunity and the space for the dye molecules to adhere; and it precipitates those dyes which, like methylene blue, give insoluble iodides. The best results are obtained if the bleaching bath contains a large excess of iodide. It not only renders the silver more receptive to dye fixation but increases its transparency by dispersion and solution. The use of iodide is limited only by its solvent action on the gelatin and the image. If pure dye colors, unobscured by the residue of iodide, are required, fixation is employed after the gelatin has been dyed and hardened with tannic acid to prevent diffusion as the mordant is withdrawn by hypo.

There are many extensions of Traube's method: Images of silver sulfide, silver, copper, and uranium ferri- and ferrocyanides, lead, tin, cobalt, and chromium salts, among others, have been used to fix dyes.

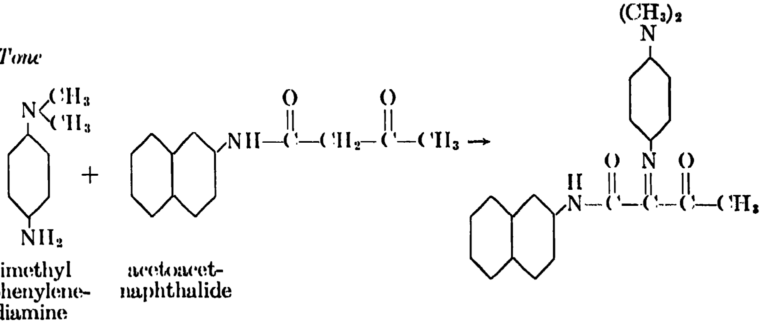
Toning by Direct and Indirect Color Development

The production of dyes directly in development was suggested by Fischer and Siegrist.[42] This process, which is discussed at greater length in Chapter X, p. 393, is of especial importance in connection with processes of color photography such as Kodachrome. It has also been used for making toned prints. It depends upon the fact that the oxidation products of certain developing agents, namely, aminophenols and *p*-phenylenediamines, couple under suitable oxidizing conditions with phenols, amines, and methylenic compounds, and produce dyes. A few equations for typical reactions occurring in the formation of various colors in dye coupling development are given directly below:

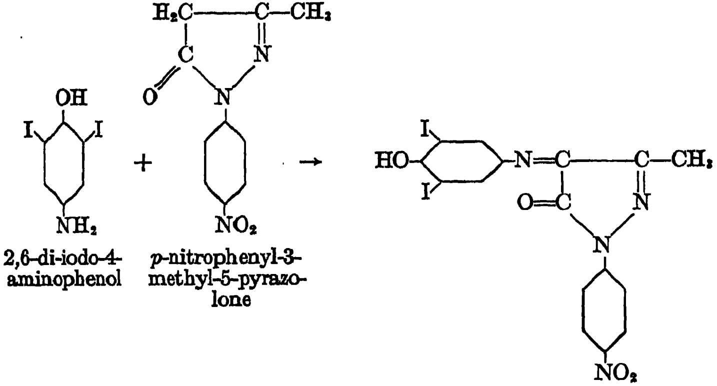
Blue Tone



Yellow Tone



Red Tone



2,6-di-iodo-4-aminophenol

p-nitrophenyl-3-methyl-5-pyrazolone

A large number of dye coupling compounds have been prepared, so that a wide range of colors can be obtained by proper selection of developing agent and coupler. Colors may also be blended by the use of mixtures of couplers or processing the emulsion successively in two or more different dye coupling developer baths.

The preparation of toned images on either film or paper by these reactions may be accomplished in one of two ways: (1) By direct development of the latent image, or (2) by bleaching the black-and-white image in ferricyanide and redeveloping in the dye-forming solution.[43]

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PART IV

SENSITOMETRY

Soon after the introduction of dry plates, photographers felt an acute need for a method of measuring sensitivity. The methods adopted were based upon *actinometers* used to determine the actinic intensity of the light used in printing processes. A number of actinometers or photometers had been designed particularly for use in the carbon process and consisted generally of a series of superposed layers of paper with numerals printed on them. When the carbon tissue was exposed under the negative, a piece of albuminized paper was exposed simultaneously under the actinometer and the exposure continued until a number corresponding to an estimate of the density of the negative was printed visibly on the albumin paper. For comparing the sensitivity of negative plates, similar actinometers made up of layers of paper were used, and to these the term *sensitometer* was applied.

In 1881, a committee of the "Photographic Club" in England was formed to choose a standard sensitometer. That adopted was the one suggested by L. Warnerke and consisted of a glass plate having on its surface twenty-five squares steadily increasing in opacity. These squares were formed as a cast in gelatin from an original produced by superimposing sheets of paper, the casting method being that known in photography as *Woodburytype.* The proportion of neutral black and gelatin used for making the cast was intended to be such that an increase of three numbers would represent a halving of the light; the actual tablets made, however, probably approximated to this only very roughly. As his standard light source, Warnerke used a phosphorescent plate made from calcium sulfide which was activated by burning an inch of magnesium ribbon close to it and waiting sixty seconds before giving an exposure of sixty seconds with the graduated tablet in contact with both the phosphorescent plate and the material to be tested.

Before the introduction of this instrument, the speeds of gelatin dry plates had been stated generally as a multiple of the speed of a collodion wet plate taken as a standard; and plates were stated to be 30, 40, 50, or 60 times as fast as a wet plate. After the general adoption of the Warnerke sensitometer, the sensitometer numbers were often marked upon boxes of plates, so that a plate might be marked "Sensitometer No. 19." The identification of brands of plates by numbers probably owes its origin to this early method of designating plate speed.

A revival of the Warnerke sensitometer was found in the photographic plate tester suggested by Chapman Jones,[2] in which a series of graded densities, prepared by casting gelatin as in the Woodburytype process, was combined with some colored filter patches to furnish an indication of the color sensitivity of the plate. The light source used with the Chapman Jones plate tester was a standard candle.

In 1919, Eder[3] introduced the Eder-Hecht wedge, first proposed by Goldberg,[4] in which a continuous wedge of neutral tinted gelatin is employed, color filters being superimposed upon it at the sides and a scale of numbers being printed on it to identify the density at different points. On each Eder-Hecht wedge is marked a wedge constant, which specifies the change of density for 10° (1 cm.) of the wedge, and in the so-called *normal* instrument this wedge constant is stated to be 0.401. It is probably necessary to determine the wedge constant of each instrument experimentally. The density characteristics of the Eder-Hecht wedge were studied by Hnatek.[5]

While other instruments of the same type have, no doubt, been used, the Warnerke sensitometer, the Chapman Jones plate tester, and the Eder-Hecht wedge are fairly representative of sensitometric tablets.

The first photographic investigator to place his measurements on a strictly quantitative basis was W. deW. Abney, who gave plates a graduated series of exposures, measured the transparency of the deposits obtained after development, and plotted curves of the relation between the transparency and the exposure (Chapter V, p. 200). The foundations of modern sensitometry, however, were laid by Hurter and Driffield in their paper of 1890 entitled "Photo-Chemical Investigations."* In order to use their exposure calculator, which they termed an *actinograph*, they found it necessary to determine the sensitivity of the plates which they used, and they began a series of researches which were published in the paper mentioned above. They established first the relation between the mass of silver deposited in a negative and the light transmitted by it and found that the logarithm of the reciprocal of the transparency, which they termed the *density*, is proportional to the mass of silver per unit area.* As a light source, they adopted at first the standard candle; in their later work, the pentane lamp. Graduated exposures were made by means of a rotating sector wheel in which successively increasing angular apertures had been cut, and the density of the developed plates was measured by means of a short bench photometer using a grease spot or, later, a Lummer-Brodhun head.

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* This account of Hurter and Driffield's work overlaps that given in Chapter V, p. 201. An account of the same work in relation to development is given in Chapter XI, p. 402. This repetition seems necessary owing to the great importance of the work and the different viewpoints involved.

If the density of the developed image is measured and plotted as a function of the logarithm of the exposure, the characteristic curve shown in Figure 214, p. 700, is obtained. An appreciable portion of the D log E characteristic curve of most photographic materials is (within the limits of experimental measurement) a straight line, which in the case shown extends from A to B. This is known as the region of *correct exposure*, because the density is directly proportional to the logarithm of the exposure, and the exposure values rendered on this portion of the curve are directly proportional to the corresponding brightness values in the object. In the lower portion of the curve, C to A, this direct proportionality does not exist; this region is referred to as the *underexposure region*, or *toe*. Likewise, in the upper portion of the curve, B to D, the direct proportionality between density and the logarithm of the exposure is not maintained, and this region is commonly referred to as the *overexposure region*, or *shoulder*, of the curve. When the straight-line portion of this curve is extended to meet the exposure axis, the point of intersection (X) is (termed by Hurter and Driffield) the *inertia* point. They found that, for the developers they used, containing no free bromide, this point remained unaffected by the time of development; and they regarded it as a characteristic of the material. Hurter and Driffield, therefore, defined the speed of a photographic material as the reciprocal of the inertia multiplied by 34, this constant being selected for use with the actinograph to give suitable exposures.

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* But, see Chapter V, p. 226.

The "H and D speed" thus measured was slowly adopted by photographic manufacturers as a measure of the sensitivity of their products, and it finally became customary in England to mark a number, supposed to be measured according to the specifications of Hurter and Driffield, upon boxes of plates. The numbers so published, however, were not always determined according to the specifications laid down by Hurter and Driffield and, in some cases, at any rate, must be considered actually misleading.

In Germany, the first commercial rating of photographic plates was in *degrees Scheiner.* The Scheiner sensitometer was introduced by Professor J. Scheiner[6] and used by him for the determination of the threshold sensitivity of plates used for astronomical photography. The original design was modified by Eder,[7] who worked out a complete system of sensitometry based on the use of the characteristic curve, the density being plotted against the logarithm of the exposure. The light source was a kerosene lamp with a flame of constant height, from which a portion was selected by a horizontal slit. Its intensity was $\frac{1}{13.2}$ Hefner candle or, since the Hefner candle = 0.9 international candle, the candle power was 0.068. This lamp was placed one meter from the exposure plane, and the sector wheel was rotated for 60 seconds at 400 to 800 r.p.m. In the sector wheel (Figures 153 *A*, *B*), each successive aperture decreases in the ratio of 1 to 1.26, so that the aperture marked *11* gives 10 times less exposure than the aperture marked *1*, and an increase of three steps corresponds approximately to a halving of the exposure. The total exposure time for the number 1 step is 16.6 seconds, and the exposure for this step is, thus, 1.14 m.c.s. A material having a Scheiner speed of 20° is, thus, one having a threshold sensitivity (to light of the quality of a kerosene flame) of 0.011 m.c.s.

The use of the Scheiner *degrees* for rating photographic materials in Germany had the same fate as that which befell the commercial application of the Hurter and Driffield speeds in England. Manufacturers found it necessary to mark their materials with ever-increasing speed numbers because of the commercial and advertising value which became attached to high speed ratings until, eventually, the system became discredited; this is often referred to by German writers as the "Scheiner inflation."

To deal with this unsatisfactory situation, a committee in Germany worked out, in 1931, the method which has become known as the DIN System.[8] It has been adopted as the German national standard system of sensitometry, but it has not been approved by other countries. In carrying out the method, a plate or film strip is exposed in a sensitometer behind a neutral gray step tablet having 30 steps and a density increment of 0.1

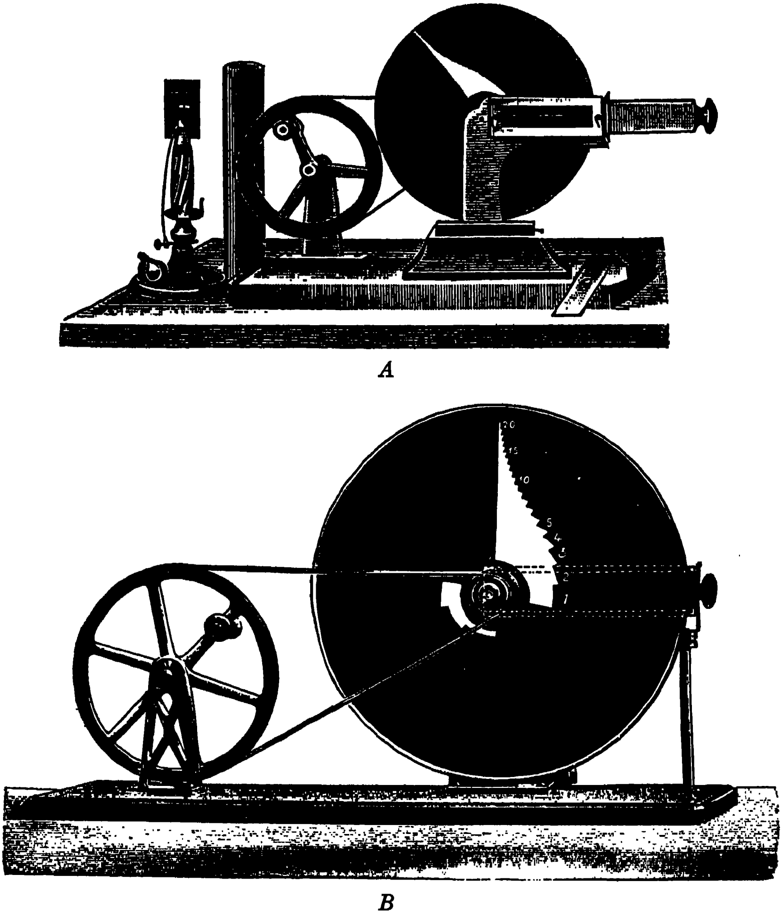

FIG. 153. Scheiner sensitometer: *A*, original form; *B*, as modified by Eder.

from each step to the next. Each step carries a number equal to its density. Exposure is nonintermittent and, in the approved apparatus, is achieved by allowing a metal plate having a slit in it to fall in front of the test strip. The exposure time is 1/20 of a second, and the light source is the Davis-Gibson light source-filter combination approved by the International Congress of Photography. After exposure, the strip is developed in a specified metol-hydroquinone developer for such a time and temperature that the maximum speed number is attained. The speed is specified as "Degrees DIN" and is determined by selecting the step on the test strip at which the density is 0.10 higher than the neighboring fog density. Figure 154 shows a print from such a test strip. If the number on the strip is, say, 1.4, then the sensitivity is indicated as 14/10° DIN.

A serious objection to this system lies in the fact that very frequently, to attain the maximum speed number, development must be carried to an extent which gives contrasts much higher than are used in normal practice. As will be seen later, the relative speed values obtained by this method do not agree with practical results as closely as the results given by later methods (Chapter XIX, p. 727).

An appraisal of the applicability of these various methods to rating the sensitivity of photographic materials involves the whole question of tone reproduction and of the interpretation of the results of precision sensitometry and must be deferred to a later chapter, in which those problems are discussed. First, however, it is desirable that the experimental methods used in the determination of the sensitometric characteristics should be dealt with in detail.

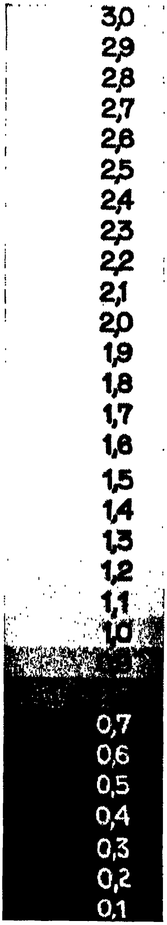

Fig. 154. Developed test strip for the DIN system.

The transition from the early methods of judging sensitivity by exposure to a graded tablet to precise sensitometry based fundamentally upon the methods of Hurter and Driffield involves five standardized conditions: (1) A light source emitting radiation of known intensity and spectral composition; (2) a means of producing graded exposures of known relative values; (3) standardized development conditions; (4) a method of measuring accurately the quantitative value of the developed image; (5) a method of interpreting the results either in the form of curves, numerical constants, or other suitable methods of expression.

SENSITOMETERS

Instruments for impressing on a photographic material a series of precisely known graduated exposures are called *sensitometers.* The essential elements of a photographic sensitometer* are shown in Figure 155, which represents a schematically generalized diagram. A light source of known *luminous intensity* emitting radiation of known *spectral composition* is represented by S. This is placed at a fixed distance from the exposure plane, R. The surface of the photographic material, P, to be tested is made to coincide with this exposure plane, being held therein by some convenient arrangement. Between the exposure plane and the light source is located an exposure-modulating device, M. The effective size of the light source and the distance are usually so chosen that the illumination incident upon the exposure plane can be computed by means of the inverse square law, the luminous intensity (candle power) of the source being known.

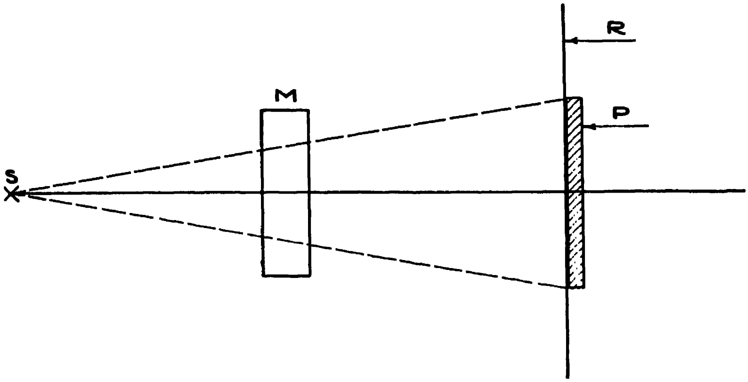

FIG. 155. Essential elements of a sensitometer.

---

* Enclosed instruments, incorporating the light source, exposure modulator, and material holder, suitable for use in a lighted room, were introduced by Sheppard and Mees.[8]

Moreover, the size of the photosensitive surface to be illuminated as related to the distance should be such that the illumination is the same at all points on the photosensitive surface to be exposed. Under these conditions, assuming that the exposure-modulating device is removed, the entire surface of the photosensitive material will be uniformly illuminated; and, if the illumination originating at the light source is allowed to act for a fixed time, every point on the photosensitive surface will receive the same exposure. The function of the exposure modulator, *M*, is to alter this condition in such a manner that various areas of the photosensitive surface are subjected to a series of *different* exposures which can be precisely predetermined.

Light Sources

The characteristics of the light source used for the determination of speed values are of utmost importance. Its *luminous intensity* must be precisely known, and it should be possible to maintain this at a constant value over long periods of time. Of equal, or perhaps greater, importance is the *spectral composition* of the radiation emitted by the source. This also must be accurately known, constant, and of very definite quality, if the final results are to be of practical use.

In selecting a light source for photographic sensitometry, it was quite natural that workers in this field should turn to standard light sources that had already been developed for the establishment of the unit of luminous intensity. In Great Britain, a standard candle, the British Parliamentary Candle,[10] was defined in the Metropolitan Gas Act of 1860 and for many years was the officially accepted unit of luminous intensity. This candle was made of spermaceti wax to specified dimensions and had a wick of specified material and size. Operated as a standard candle, it burned 120 grams of spermaceti an hour. In their early work, Hurter and Driffield [11] adopted this unit of luminous intensity as the light source for sensitometry. The standard candle did not continue to meet the requirements as a standard of luminous intensity on account of its lack of reproducibility. It was superseded (1898) by the pentane lamp devised by G. A. Vernon-Harcourt,[12] which burns a mixture of pentane vapor and air in a wickless burner. In the final form which was adopted in England as an official standard for testing illuminating gas, a larger form was used, which gave a luminous intensity of 10 candle power. This source was used by Hurter and Driffield in their later work. In Germany, the Hefner lamp, which was invented in 1884 by F. von Hefner Alteneck,[13] was adopted as the official unit of luminous intensity and is still the official standard in that country. This lamp, the prototype of which is maintained by the Physikalische Reichsanstalt, burns pure amyl acetate. In Germany, Scheiner and his followers adopted this light source for use in photographic sensitometry though Eder replaced it by the flame of a kerosene lamp (p. 591).

In 1895, Violle[14] proposed the use of an acetylene flame as a standard of luminous intensity, and this was employed by Sheppard and Mees[15] in their investigations. The first burners used gave a flat (fish-tail) flame, and in front of this was placed a shield with a square opening. This burner did not prove satisfactory because it was very sensitive to air drafts and to the pressure of gas. Sheppard and Mees[9] therefore adopted a type of acetylene burner giving a cylindrical flame similar to that suggested by Fèry.[16] The brightness varies somewhat from top to bottom; but, of a considerable portion, approximately halfway between the tip and the base of the flame, the luminous intensity per unit area is very constant. If a screen or diaphragm is placed very close to the flame itself, a section can be isolated which serves as a fairly satisfactory standard light source.

The characteristics of this light were investigated by Jones,[17] who found that by setting the window at the proper height above the burner tip and operating the flame at a pressure of 9 cm. of water, its sensitivity to changes in gas pressure is slight, being only 0.15 per cent for a change in gas pressure of 2 per cent. A cross section through this burner with its protecting hood and the re-entrant window for the isolation of the most satisfactory part of the flame is shown in Figure 156. Long experience has shown that this burner, if properly operated, is sufficiently precise and reliable for purposes of photographic sensitometry. It is not a reproducible standard and hence must be calibrated by comparison with certified standards of candle power obtained from standardizing laboratories, such as the National Bureau of Standards or the National Physical Laboratory. It has one advantage over standardized electric incandescent lamps in that the equipment required for the operation of the source under controlled conditions is very simple, consisting only of a water manometer and needle valve, by means of which the gas pressure can be maintained at 9.0 cm. of water. The acetylene gas supplied to the burner must, of course, be carefully purified and free from water vapor. Experience has shown that generators in which the calcium carbide is added to the water are more satisfactory than those in which the water is added to the carbide. This is due probably to the fact that in the former case the gas is generated at a lower temperature than in generators of the second type and, hence, the admixture of impurities is somewhat less. Another great advantage of the acetylene flame is the fact that, under the controlled conditions specified above, it emits light of constant spectral composition. It is only necessary, therefore, to standardize the source as to its luminous intensity.

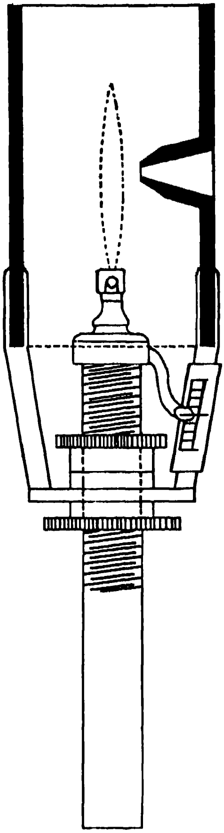
FIG. 156. Standard acetylene burner.

An important advance in the standardization of the unit of luminous intensity was made in 1909, when, as a result of international agreement between the standardizing laboratories of Great Britain, France, and the United States, a group of incandescent electric lamps were specified as having definite candle-power values. These lamps, of course, were not primary standards of luminous intensity, since they were not reproducible to specifications and none of the lamps actually had a candle power of one international candle. In effect, therefore, the unit of luminous intensity, the international candle, was a unit of arbitrarily chosen magnitude (equivalent approximately to the discarded British standard candle), which was maintained by means of these carefully preserved groups of standardized incandescent lamps. Germany and other countries which had adopted the Hefner standard continued to use that unit. It was agreed, however, to take the value of its luminous intensity as exactly 0.9 of the international candle.

For various reasons, all the standards mentioned thus far have been unsatisfactory; the flame standards because of their lack of reproducibility and the incandescent tungsten lamps because they could not be reproduced to specifications. It has long been realized that, if certain technical difficulties could be overcome, a *black body* radiator would make an ideal candle-power standard because such a radiator is independent of the material of which it is constructed and depends only on its temperature. These difficulties were overcome and, in 1940, by international agreement, the standard of luminous intensity became a black body operating at the temperature of freezing platinum (2046.6° K.). Such a black body has by definition a brightness of 60.0 *new* candles/cm.^{2} The Hefner candle continues to be exactly 0.9 of this new international candle. This change in standards makes little practical difference because the new candle is slightly less than 2 per cent brighter than the older candle based on the incandescent lamps, a difference only slightly greater than the limits of photometric error.

In practice, either for practical photometric measurements or for use in sensitometry, carefully calibrated electric incandescent lamps are superior to any other form of illumination because of the lack of reproducibility of the flame standards and the experimental difficulties involved in setting up a black body standard. The temperature at which an incandescent filament operates is, of course, dependent upon the impressed voltage. Since the quality of radiation emitted by an incandescent solid is dependent upon the temperature of that material, it follows that the spectral composition of the radiation emitted by an incandescent lamp depends upon the current flowing through the filament. In using calibrated incandescent lamps for photometric measurements, it is necessary, therefore, for their calibration to include not only their luminous intensity but also the temperature at which they operate.

While many modern incandescent tungsten lamps operate at filament temperatures as high as 3400° K., it is impossible to calibrate them satisfactorily at such a temperature. The lamps previously used by the national standardizing bureaus for the maintenance of the international candle were operated at filament temperatures not much in excess of 2400° K. The effective equivalent temperature of sunlight at the earth's surface is approximately 5400° K. It is obvious, therefore, that with electric lamps it is impossible to obtain radiation approximating in quality that of sunlight.

The quality of the radiation due to the incandescence of solids such as a tungsten filament or the finely divided carbon particles in a flame can be defined as the temperature of a black body

TABLE LXII

Color Temperature Values of Photometric Standards and Practical Light Sources

Source	*Color Temperature*
A. *Standards of Luminous Intensity*	
Standard British Candle	1930° K.
Hefner Lamp	1880° K.
Harcourt Pentane	1920° K.
Acetylene (E.K. Standard)	2415° K.
Incandescent Carbon (4 w.p.c.)	2080° K.
Incandescent Tungsten (1.25 w.p.c.)	2400° K.
Black Body at Freezing Point of Platinum	2046.6° K.
B. *Standards of Spectral Quality*	
Sunlight (Washington Mean Noon)	5400° K. Photographic Standard
International Commission of Illumination Illuminant A	2848° K. Vis. Tungsten
International Commission of Illumination Illuminant B	4800° K. Vis. Sunlight
International Commission of Illumination Illuminant C	6500° K. Vis. Daylight
C. *Practical Sources of Illumination*	
Noon Sunlight	5400° K.
Daylight	6500° K.
Skylight	12,000 to 18,000° K.
Crater of Carbon Arc (ordinary hard cored)	4000° K.
White Flame Carbon Arc	5000° K.
High Intensity Carbon Arc (sun arc)	5500° K.
40-watt Tungsten Incandescent Lamp 10.7 lumens/watt	2760° K.
500-watt Tungsten Incandescent Lamp 19.6 lumens/watt	2960° K.
1500-watt Tungsten Incandescent Lamp 22.0 lumens/watt	3225° K.
1000-watt Tungsten Incandescent Photoflood 31.6 lumens/watt	3360° K.
250-watt Tungsten Incandescent Photoflood 35.8 lumens/watt	3475° K.

which has the same distribution of energy in the visible spectrum as the source under consideration. This is known as the *color temperature* of the source. In Table LXII are given the color temperatures of various standard light sources which have been used in photographic sensitometry and also those of various sources used in practical photography.

The basic reason it is so important that the spectral composition of the radiation emitted by any source to be used as a standard of photographic intensity shall be known and appropriate is that photographic materials do not have the same spectral sensitivity as the retina of the human eye, which is used in the evaluation of the luminous intensity of any light source. Moreover, the spectral sensitivities of photographic materials differ enormously among themselves (Chapter XXIII). Figure 157 shows the spectral sensitivity curves of three typical photographic materials, namely: *A*, ordinary or blue-sensitive materials; *B*, orthochromatic, blue- and green-sensitive materials; and *C*, a panchromatic material. *D* is the spectral sensitivity curve of the average normal human eye, this curve being frequently referred to as the *visibility curve.*

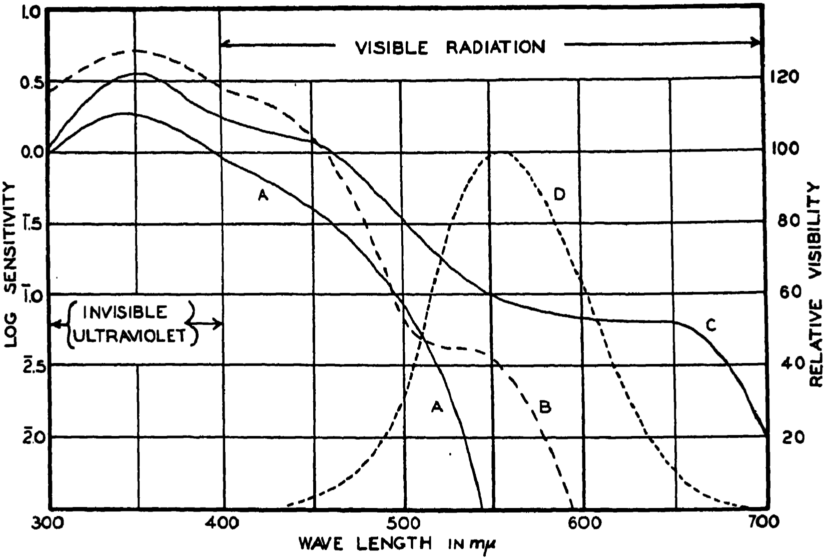

FIG. 157. Spectral sensitivity curves of the eye and of three typical photographic materials.

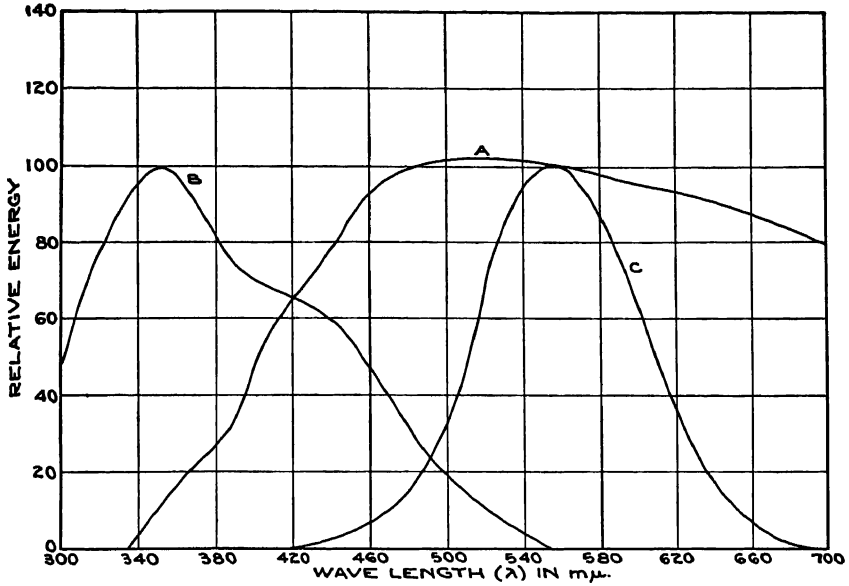

FIG. 158. Energy distribution of sunlight with sensitivity curves of the eye and of unsensitized photographic material.

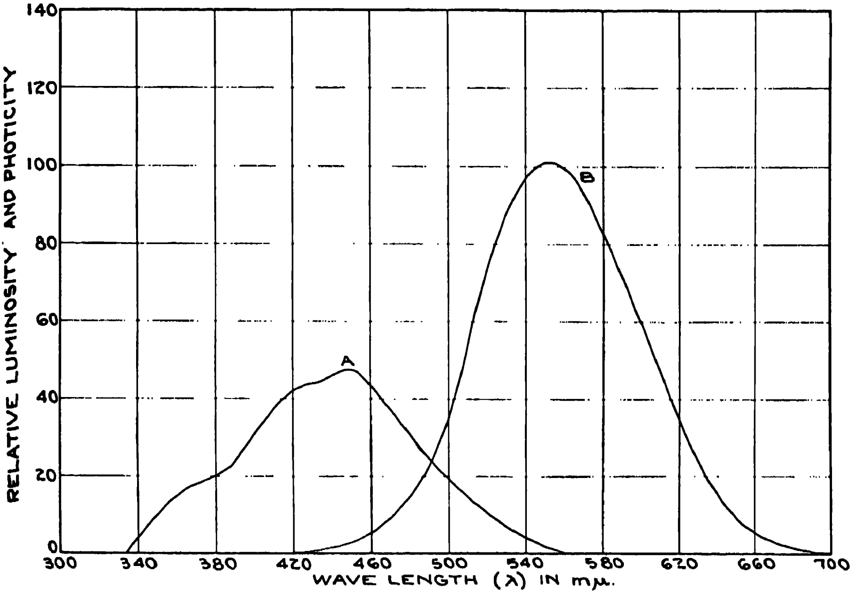

FIG. 159. Relative effectiveness of sunlight for the eye and for unsensitized photographic material.

The sensitivity of a photographic material is expressed in terms of the exposure which produces some definite response. Exposure is expressed in terms of illumination units, *e.g.*, meter-candle-seconds, the "candle" being measured *visually*. In Figure 158, Curve *A* shows the energy distribution in average noon sunlight; Curve *B*, the spectral sensitivity curve for ordinary blue-sensitive material; and Curve *C*, the visibility function for the human eye. If the ordinates of Curves *B* and *C* are multiplied by those of Curve *A*, the curves shown in Figure 159 are obtained, of which the relative areas indicate the relative effectiveness of the same light source (sunlight) for the eye (Curve *B*), and for the blue-sensitive materials (Curve *A*). It is seen that the relative effectiveness of two light sources depends upon their energy distributions (color temperature) and upon the spectral sensitivity of the materials. In Table LXIII are shown relative speed values as determined with a 2360° K. source and a 5000° K. source for three materials differing in color sensitivity. The ratios of the speed values of the materials for the two sources are shown in column *F*.

TABLE LXIII

THE EFFECT OF COLOR TEMPERATURE OF STANDARD SOURCES UPON SPEED VALUES OF VARIOUS PHOTOGRAPHIC MATERIALS

	Color Temperature of Source					
	5000° K.		*2360° K.*			
Materials	*1/i*	*RS*	*1/i*	*RS*	ΔRS(%)	*F*
Ordinary	63	100	18	100	00	3.5
Orthochromatic	42	67	17	94	+40	2.5
Panchromatic	33	52	17	94	+81	1.9

The spectral sensitivity of different materials classed ordinarily as *blue-sensitive* (that is, non-color sensitized) varies sufficiently to show serious differences in speed if measurements are made with sources of low and high color temperature. This is illustrated in Table LXIV. A standard for use in sensitometry must therefore be of such a quality that the values of sensitivity obtained will be most useful for the purpose for which the work is being done. While, undoubtedly, a large proportion of photographic material is exposed under artificial lighting, it seems probable that a larger proportion is exposed to light of sunlight quality. Moreover, many of the artificial sources are of the high color temperature type, such, for instance, as the flame arcs. For the sensitometry of negative materials, it is therefore highly desirable to adopt a source of high color temperature duplicating as closely as possible mean noon sunlight.

Reference to the table of color temperatures (Table LXII) shows that no satisfactory standard of luminous intensity is available which even remotely approaches sunlight in spectral composition. It is necessary, therefore, to use a selectively absorbing filter between the light source and the exposure plane.

TABLE LXIV

THE EFFECT OF COLOR TEMPERATURE OF STANDARD SOURCES UPON SPEED VALUES OF VARIOUS PHOTOGRAPHIC MATERIALS

	Color Temperature of Source					
Ordinary (Blue-sensitive)	*5000° K.*		*2360° K.*			
Materials	*1/i*	*RS*	*1/i*	*RS*	Δ*RS*(%)	*F*
A	63	100	18	100	00	3.5
B	63	100	15	83	−17	4.2
C	50	79	18	100	+27	2.8
D	46	73	16	89	+22	2.9
E	44	70	14	78	+11	3.1
F	23	37	8	44	+19	2.9
G	10	16	4	22	+37	2.5
H	3.5	5.6	1.2	6.7	+18	2.9

For many years, the cylindrical acetylene flame standard, previously mentioned, was used in combination with a dyed gelatin filter (Wratten No. 79). The radiation from this source-filter combination matches very closely in color that from noon sun. Spectrophotometric examination of the transmitted radiation shows that the match is only a subjective one and that there is an appreciable departure from the actual spectral distribution of radiation in mean noon sunlight. The departure, however, is not serious from the practical standpoint; in fact, speed values determined with this source-filter combination using materials differing widely in spectral sensitivity agree very well with speed values determined by using actual sunlight. The filter mentioned is very stable, but it is not precisely reproducible as a primary standard. It was, therefore, a notable advance when Davis and Gibson[18] developed a liquid filter consisting of two solutions which, combined with either acetylene or a standard tungsten lamp operating at 2360° K., duplicates mean noon sunlight very precisely. In Figure 160, curve *T* shows the spectral transmission of this filter. If the filter is used with an incandescent tungsten lamp operating at a color temperature of 2360° K. (or with the standard acetylene burner) having the distribution of energy shown in Curve *E*, the spectral distribution is that indicated by the small circles (Figure 160). The solid curve, designated as *E′*, represents the spectral quality of mean noon sunlight at the earth's surface. It is seen, therefore, that the source-filter combination gives a good approximation to radiation of sunlight quality. These filters are reproducible with high precision and have good stability. They represent, in fact, the most satisfactory means of realizing in the laboratory radiation of sunlight quality for sensitometric purposes.

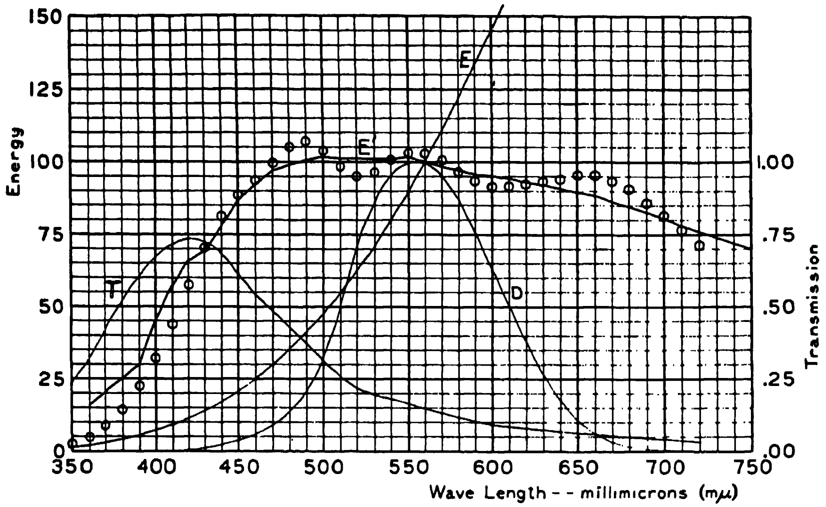

FIG. 160. Spectral quality of sunlight and screened tungsten.

The International Unit of Photographic Intensity

The International Congress of Photography for some years attempted to standardize a satisfactory unit of photographic intensity. Finally, at the seventh congress, which met in London in 1928, a resolution was passed adopting a 2360° K. source screened with the Davis-Gibson liquid filter as a means of realizing the international unit of photographic intensity, which is defined as one visual candle power of radiation of the quality emitted by the source-filter combination mentioned above. The Davis-Gibson filter for use with 2360° K. source is made according to the following formula:

Solution A

Copper sulfate ($CuSO_4 \cdot 5H_2O$)	3.707	gm.
Mannite ($C_6H_8(OH)_6$)	3.707	gm.
Pyridine (C_5H_5N)	30.0	cc.
Water (distilled) to make	1000	cc.

Solution B

Cobalt ammonium sulfate ($CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$)	26.827	gm.
Copper sulfate ($CuSO_4 \cdot 5H_2O$)	27.180	gm.
Sulfuric acid (sp. gr. 1.835)	10.0	cc.
Water (distilled) to make	1000	cc.

THE MODULATION OF EXPOSURE

Since exposure may be modulated by control of either the intensity of the light or the time of exposure, sensitometers may employ either an intensity scale or a time scale. The earliest sensitometers employed an intensity scale; thus, the Warnerke tablet was made of squares of pigmented gelatin forming a scale of densities.

Optical Wedges

Optical wedges and light-absorbing tablets, made by casting gelatin containing dyes or colloidal carbon, can be used for the modulation of exposure in sensitometers and the measurement of light intensities in photometers and densitometers. The problem in their use is to modify the intensity in a known manner through a wide range without affecting the quality of the light transmitted. In practice, this is almost impossible; even if wedges are uniform in absorption for visible light, they almost always show selectivity in the ultraviolet and infrared. Consequently, when heterogeneous light is used, there is some doubt as to the real absorption coefficient; it must be determined photographically with light of the same composition as that employed in the photometric work. A change of absorption with wave length is of small importance in work on the spectrum, since it is easy to employ a different constant for each wave length. For work in the ultraviolet, it is necessary to use quartz instead of glass to hold the gelatin wedge, and Toy[19] showed that such wedges could be used to about λ300; but the absorption coefficient increased so rapidly with decreasing wave length that they were useless at shorter wave lengths. However, absorbing wedges have been made, of which the constant changes slowly with wave length[20] and which can be used down to λ240.

The use of absorbing media has been studied very extensively by Dobson, Griffith, and Harrison.[21] They employ an optical wedge which may consist of a wedge-shaped piece of neutral gray glass cemented to a similar piece of clear glass to form a parallel plate or may be made of gelatin containing either a mixture of dyes approximating a neutral gray or metallic silver. The theory of the optical wedge as stated by Dobson, Griffith, and Harrison is as follows:

> "Consider first a layer of absorbing material of unit thickness, and let I_0 be the intensity of radiation incident normally on the layer. Suppose that in passing through the layer I_0 is reduced to AI_0, where A is some fraction depending on the material and the wave length of the radiation. Each unit thickness of the medium reduces the intensity of the radiation which passes through it by the fraction A, so that after passing through x units, I_0 becomes A^xI_0; and
>
> $$I = I_0 10^{-ax}$$
>
> where
>
> $$a = \log \frac{1}{A},$$
>
> a is the absorption coefficient of the medium for the given wave length.
>
> "Now consider radiation passing normally through the wedge.
>
> "At one extreme end of the wedge, the thickness of absorbing material is zero (neglecting the absorption of the glass), so that the radiation passes through unchanged in intensity. But at a distance y from this end the radiation passes through a thickness x which is proportional to y. Therefore,
>
> $$I = I_0 \times 10^{-ax} = I_0 \times 10^{-Ky}$$
>
> or
>
> $$\log I = \log I_0 - Ky.$$
>
> K is called the *wedge constant.*"

The preparation of neutral wedges was brought to the general attention of the scientific world by a paper published by Goldberg in 1910.[4,22] They were made of a suspension of Winsor and Newton's lampblack water color in gelatin. A prismatic mold is made of two pieces of glass allowed to make contact at one end and separated at the other by a small strip of glass of any required thickness, a convenient thickness being one millimeter. One of the glasses is coated with a solution of collodion or, better, albumin, and the dyed gelatin is allowed to penetrate between the two glasses, which are then chilled, so that the gelatin sets hard. The glass can then be removed from one side and the wedge dried. A complete description of the method is given by Goldberg in his book on tone reproduction.[23]

Materials for use in making neutral wedges have been studied by Ventman.[24] Mixtures of dyes were found to be satisfactory throughout the visible spectrum; but below 440 mμ the absorption increases considerably, while above 700 mμ it diminishes rapidly. Graphite wedges, consisting of highly dispersed graphite particles not larger than 2 μ in very dilute gelatin solutions containing a little ammonia, are useful throughout a wide range. The deviation from neutrality is 7 per cent at the shortest wave lengths but less than 2½ per cent in the deep red and infrared regions. Graphite introduces some scattering.

For much photographic work, it is convenient to use wedges consisting of a photographic image. These may be prepared by printing from an optical wedge on a material having a long straight-line portion to the characteristic curve, which can be determined by direct sensitometry, and developing the material as closely as possible to a γ of unity. Such wedges are, of course, identical in spectral distribution of absorption and scattering power with a photographic image on the same material developed in the same way. (If developed with metol-hydroquinone, they will be very nearly neutral throughout the visible spectrum and the near ultraviolet.) Such photographic wedges must always be calibrated *in situ* before use.

SENSITOMETRIC INSTRUMENTS

L. A. Jones has classified the instruments used for exposure in sensitometry into intensity-scale and time-scale sensitometers, subdivided according to the continuity or intermittency of the exposure and, finally, according to the use of continuous or stepped exposure scales:[25]

Type I. Intensity-Scale (Sensitometers)
I variable, t constant
- *A*. Exposure intermittent
  1. Wedged exposure
  2. Stepped exposure
- *B*. Exposure nonintermittent
  1. Wedged exposure
  2. Stepped exposure

Type II. Time-Scale (Sensitometers)
I constant, t variable
- *A*. Exposure intermittent
  1. Wedged exposure
  2. Stepped exposure
- *B*. Exposure nonintermittent
  1. Wedged exposure
  2. Stepped exposure

A Type II-B sensitometer is, therefore, a nonintermittent time-scale instrument.

Time-Scale Sensitometers

Time scales may be impressed either by continuous or intermittent exposures. The continuous exposure methods have many advantages but the disadvantage that the light source must be kept constant throughout the time of exposure. With the use of intermittent exposures, such as are given by a rotating sector wheel, long-period variations of the light source are of little importance, since they act upon the whole of the strip at the same time and do not affect the shape of the curve. The difficulty of obtaining light sources which did not vary in intensity induced Hurter and Driffield to adopt the rotating sector wheel; the use of a candle made it difficult to give a series of successive time exposures with any great precision. A characteristic Hurter sector wheel is shown in Figure 161. Each successive aperture is half the size of the preceding one, so that the innermost ring gives an exposure of half the total exposure; the next one, one quarter; the next, one eighth; and so on, there being nine sectors in all. Such a sector wheel must be cut with great precision, and it is generally best to check calibration upon a photometer.

Sensitometers using rotating sector wheels were in general use until about 1920, but they have the very serious fault that the exposure is intermittent and that an intermittent exposure is not integrated by photographic materials (Chapter VI, p. 250), so that the values of inertia and γ given by the characteristic curves are different for intermittent and nonintermittent exposures. This is illustrated in Figure 162, in which are shown the sensitometric curves for the same material derived from intermittent and nonintermittent exposures of identical magnitudes.

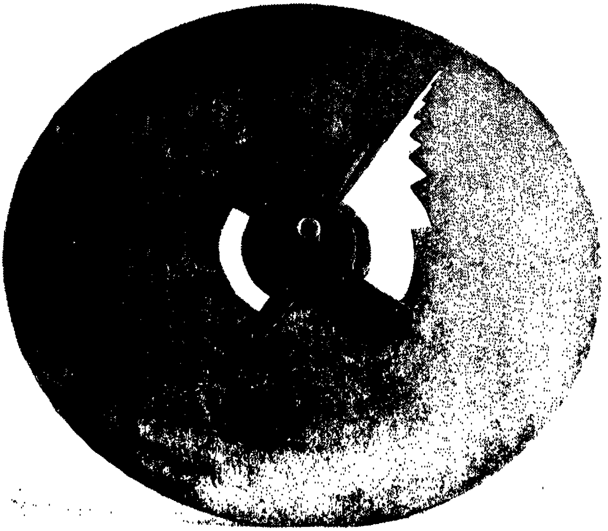

FIG. 161. Hurter and Driffield sector wheel.

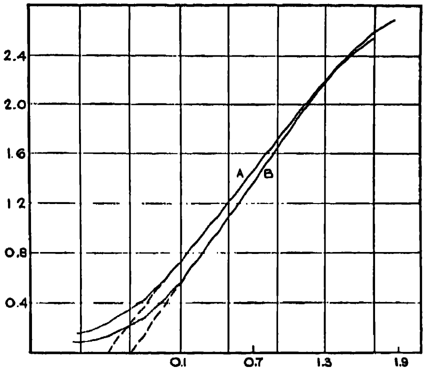

FIG. 162. Sensitometric curves from (A) nonintermittent and (B) intermittent exposures.

Since the intermittency effect is associated with the reciprocity failure (Chapter VI), it is not the same for different materials, so that the comparative values obtained on an intermittent sensitometer do not correspond to those which would be obtained if continuous exposures were given.

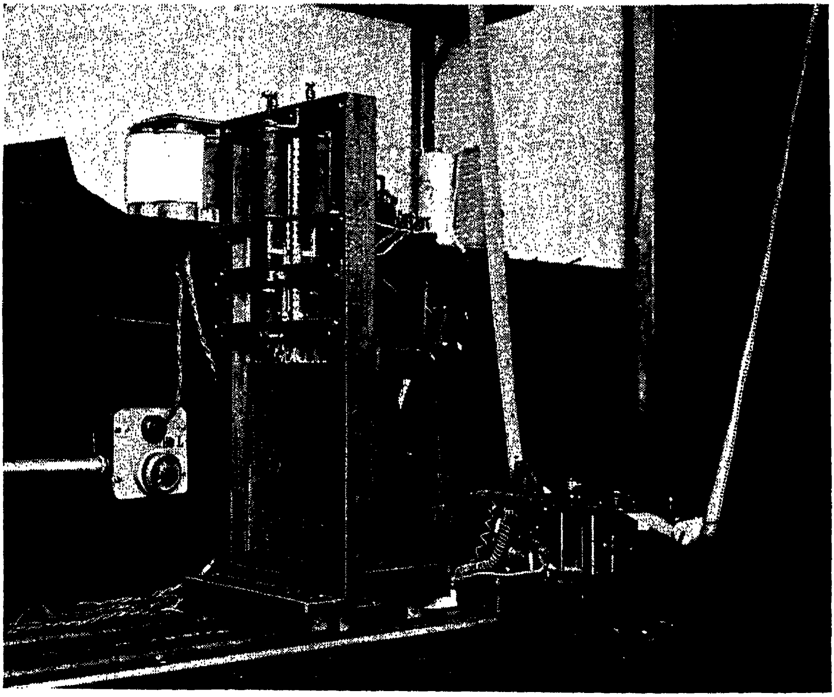

FIG. 163. Film strip operated, falling-plate sensitometer.

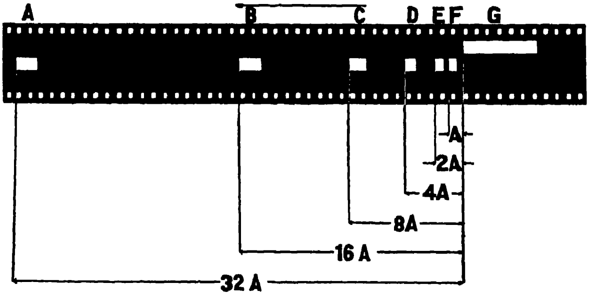

FIG. 164. Perforated film strip for operating falling-plate sensitometer.

As soon as methods were available for maintaining light sources constant in intensity over a considerable period, it was possible to abandon the rotating sector wheel type of exposure modulator and use instruments in which the exposure was continuous.

Jones used a falling-plate instrument,[25] in which the slotted plate carrying a series of apertures varying logarithmically in length is guided by vertical ways and driven at a uniform linear velocity by a motor-driven chronograph mounted on the base of the instrument. The motor used is governed, giving a relatively high precision timing. A slightly different form is shown in Figure 163. An opaque shutter is allowed to drop at predetermined time intervals in front of the photosensitive surface, cutting off the illumination incident on various areas at a series of times calculated to produce the desired time scale. The dropping of the plate is controlled by a solenoid actuated by means of the contact maker shown at the lower right-hand part of the figure. This circuit-making device consists essentially of a strip of motion-picture film in which perforations are spaced logarithmically, as shown in Figure 164. By means of a synchronous motor, this is driven at a constant linear velocity through a film gate provided with a contact-making device so that, as each aperture comes into position, an electrical contact is made, thus allowing the shutter plate to drop one step. The offset aperture, shown at *G*, operates a second contacting device, which turns on the light source at the proper instant.

A nonintermittent time-scale exposure can be obtained by a sector wheel identical in design to that used by Hurter and Driffield. It is only necessary to drive the disk at the proper angular velocity, so that the required times of exposure are obtained by a single revolution of the wheel. The opaque portion of the disk serves to protect the sensitive material while it is being placed in position in the exposure plane. The disk is then picked up by means of a suitable clutch connecting it to a driving mechanism operating continuously at a constant angular velocity, the clutch being automatically disengaged after the disk has made one revolution. This mode of operation is only feasible if the time for a complete revolution of the disk is relatively long, since it is not advisable to start the disk at a high angular velocity and stop it at the end of the exposure cycle. If it is desirable to use short exposure times, it is better to allow the sector disk to operate continuously and use a selector shutter operated in synchronism with the sector disk. Various sensitometers have been made on these general principles. One is shown in Figure 165. The sector wheel is mounted in the housing, *D*, the standard light source in the housing, *H*, and the sensitive material is held in the exposure plane by means of the plate holder, *E*. The driving mechanism, which consists of a synchronous motor, is mounted on the base at the extreme left, and a one-turn mechanism serves to pick up the sector disk and carry it through exactly one complete revolution.

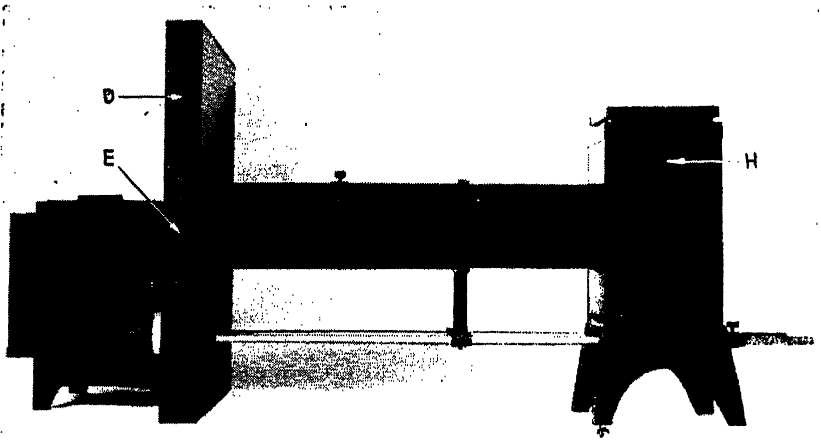

FIG. 165. Practical sensitometer using continuously moving sector disk and a selector shutter.

A sensitometer of similar design is described by Hardy.[26] The exposure time scale is extended to much shorter times by the use of one sectored disk mounted on a shaft concentrically with respect to the one driving a second disk at a lower angular velocity. A slot of relatively small angular dimensions in the larger and more slowly moving disk serves as a selector shutter, thus isolating the exposures due to a single revolution of the faster moving disk which operates at an angular speed thirty-two times as great as that of the other. The more slowly moving disk is picked up by a suitable clutch mechanism which causes it to make exactly one revolution. This sensitometer gives a time scale consisting of thirteen steps varying in exposure time by consecutive powers of 2.

A sensitometer of the one-turn sector wheel type has also been constructed and used at the National Bureau of Standards.[27] This is a very elaborate machine designed to work over a wide range of exposure times. The sector wheel runs continuously at a predetermined speed calculated to give the desired exposure times, depending upon the sensitivity of the material being tested. The exposure intervals due to a single revolution of the wheel are automatically isolated by an electromagnetic selector shutter operated by means of a commutator attached to the shaft on which is mounted the exposure time modulating shutter.

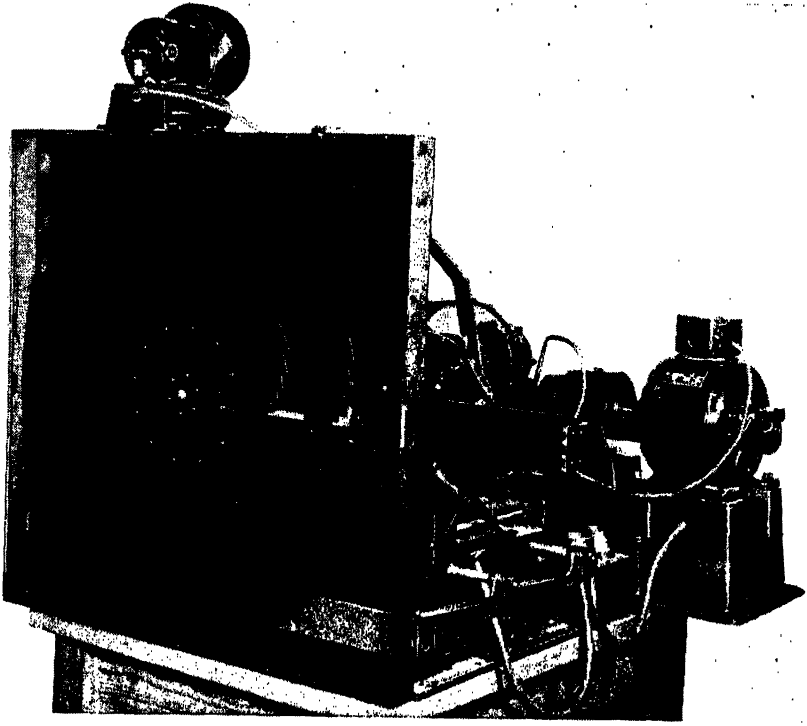

FIG. 166. Double sector wheel sensitometer.

A double sector wheel sensitometer[28] similar in design to the Hardy instrument is shown in Figure 166. This consists of two concentrically mounted sector wheels, the large one rotating at a lower angular velocity (1/16) than the smaller, inner disk. The larger disk contains a narrow aperture which serves as an automatic selecting shutter for isolating the exposures due to the inner high-speed disk. In the design of this instrument, particular attention was devoted to obtaining a high level of illumination on the sensitive material so that the exposure times could be very short and, at the same time, sufficient exposure was available. The exposure scale obtained consists of twenty-three $\sqrt{2}$ steps, the maximum exposure time being 0.512 second and the minimum exposure time 0.00025 second. The mid-step (No. 12) has an exposure time of 0.0112 second. The mid-point of the exposure scale, therefore, has a time factor of the same order as that used commonly in practical work. The sensitometric strip, in order to accommodate the twenty-three exposure steps, each of which consists of a circular area 8 mm. in diameter, must be about 10 inches long. To illuminate an area of this size uniformly and at a sufficient level to give the requisite exposure, a very high-candle-power light source would be required since it would have to be placed at a considerable distance. To avoid this, a single area of the exposure scale is illuminated by a relatively low-candle-power source placed within a few inches of the exposure plane. The various steps in the exposure scale are therefore exposed one after the other. Since the larger or more slowly moving sector disk makes one revolution in 1.8 seconds, the entire series of twenty-three steps is exposed in a total time of approximately 40 seconds. The lamp housing carrying the standard light source must be moved laterally through a distance representing the separation between consecutive steps on the scale so that, at the instant of exposure, the optical axis of the lamp house coincides with the center of the circular area to be exposed.

A sensitometer designed particularly as a control instrument for use with motion-picture film was developed by L. A. Jones and is in very extensive use in the United States.[29] It is one of the few sensitometers available commercially and is known as the *Eastman Type II-B Sensitometer.** The general arrangement of the instrument is shown in Figure 167, and a section in Figure 168. The lamp house contains a tungsten filament lamp of a precision type carefully standardized. The light from this passes through a filter and is then reflected by a mirror to the exposure plane, which is conveniently placed on top of the instrument. The sensitometer is intended to be used in a darkroom, the material being inserted in strips. The exposure modu-

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* Page 608.

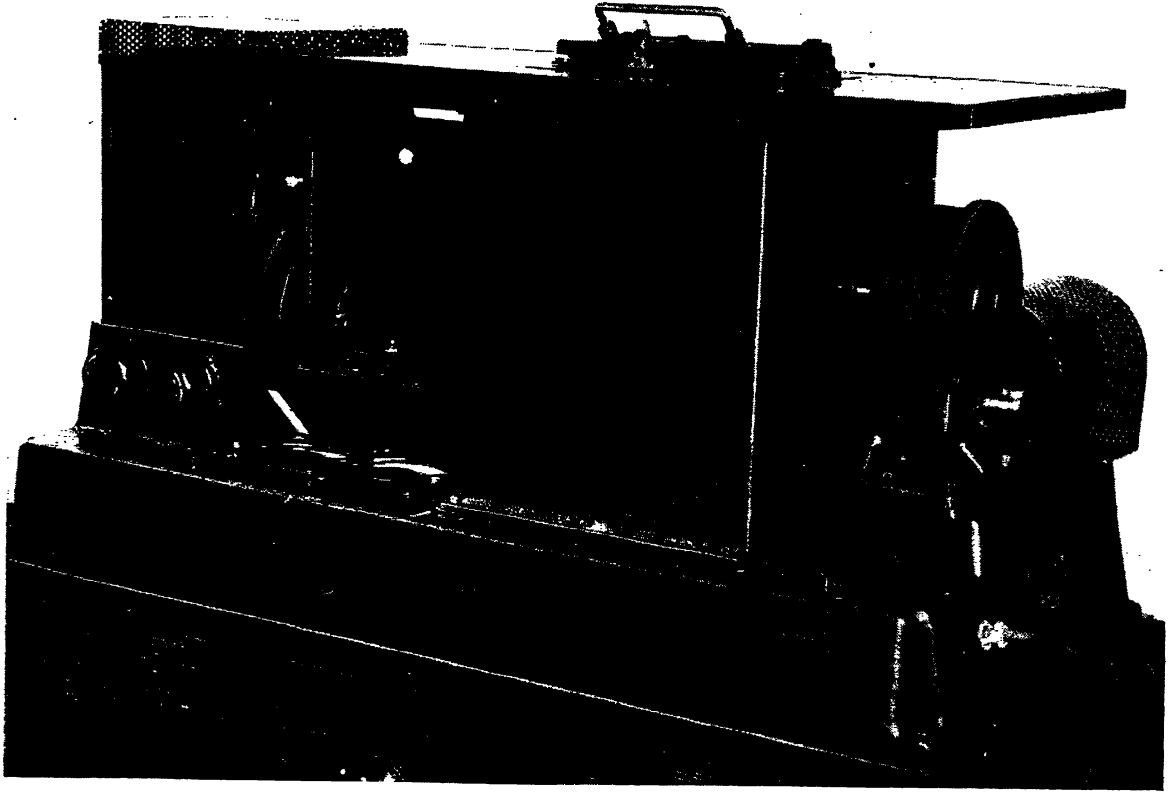


Fig. 167. Eastman Type II-B sensitometer.

lator is a cylindrical drum which is given one turn for each exposure by a motor using a reducing gear. Accuracy in the time of exposure is assured by the operation of a synchronous motor. The cylindrical drum has twenty-one apertures increasing as powers of $\sqrt{2}$. For ordinary work, gelatin compensating filters are used to correct the color of the lamps to daylight for negative materials or for positive materials to a color temperature of 3000° K., a value comparable with that used in motion-picture printers. If desired, a Davis-Gibson filter can be used instead of the cemented gelatin filter.

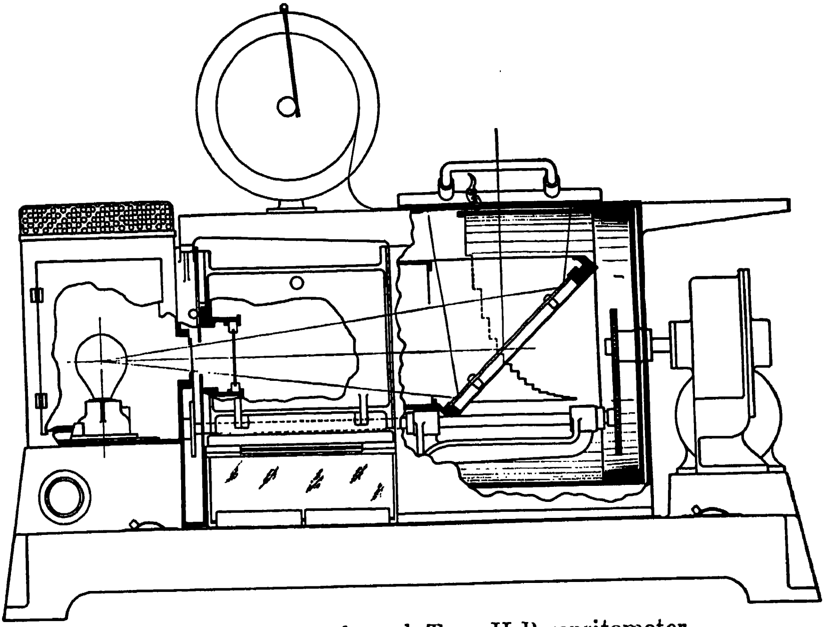


FIG. 168. Section through Type II-B sensitometer.

Intensity-Scale Sensitometers

The production of accurate step tablets and wedges makes possible the construction of very simple and efficient sensitometers operating on an intensity scale. The precision of such instruments is sufficient for general sensitometric use and, especially, for the control of photographic operations, though they are not suitable as primary instruments in a sensitometric laboratory. The tablets may also be used in sensitometers similar to those constructed with rotating sector wheels or drums. Such a sensitometer is used in the German DIN system of speed determination.

Time-scale sensitometers were adopted in practice in spite of their disadvantages because of the difficulty of obtaining satisfactory instruments using an intensity scale. Exposure-timing systems may be controlled accurately through wide ranges of time by fundamentally simple mechanical contrivances. The modulation of light intensity through the desired range involves either complicated mechanisms or intricate optical devices. Nevertheless, intensity-scale sensitometry is to be preferred as a basis of standardization and calibration of photographic materials because in practice the latter are nearly always exposed on an intensity-scale basis. The possibility of errors by the time-scale methods because of the failure of the reciprocity law, which in many cases may be of considerable magnitude, is eliminated by intensity-scale methods if the exposure times are comparable with those used in practice.

The only sensitometer which can be expected to give results corresponding to those obtained in practice is one which permits a continuous exposure at an intensity level and, therefore, of a duration approximating that obtaining when the materials are used in practical work. For negative materials, this means a high level of intensity and a short exposure. For such materials as motion-picture positive film, the same is true, but materials to be tested for use in astronomy, for instance, require a much lower level of intensity and much longer exposure. An extreme case is afforded by materials intended for use in sound recording, where the highest levels of intensity are required, since the exposure involved in recording modulated sound is of the order of 1/20,000 second.

The intensity level at which the exposure is made is of great importance in connection with the sensitometry of photographic papers. In Figure 169 are four curves showing the values of log It required to produce reflection densities of 0.2, 0.5, 1.0, and 1.5, respectively, for various values of log I. If the effective exposure were independent of the intensity, these curves would be straight lines parallel to the base. Any ordinate drawn across the curves represents a condition obtaining in time-scale sensitometry. Any line drawn across the curves at an angle of 45 degrees to the co-ordinate system gives a relation obtaining in intensity-scale sensitometry. Several of these 45-degree lines are labeled, for example, 1000 *s* or 100 *s*, corresponding to various times of exposure. The ordinate at *a* at an intensity level of log 0.9 represents a typical time-scale sensitometric measurement with a maximum time of 80 seconds. This represents the older time-scale results. The 4-second intensity-scale line represents the new sensitometric method, which is comparable with conditions of practical exposure. If the intercepts of the latter line and the iso-density curves are projected onto the ordinate *a*, marked differences on the *It* scale from the intercepts of line *a* and the iso-density curves will be seen. If the density values are plotted against the *It* scale for each group of intercepts, the characteristic curves shown in the insert of Figure 169 are obtained. These curves show the large differences which may occur between the results of time-scale and intensity-scale measurements.

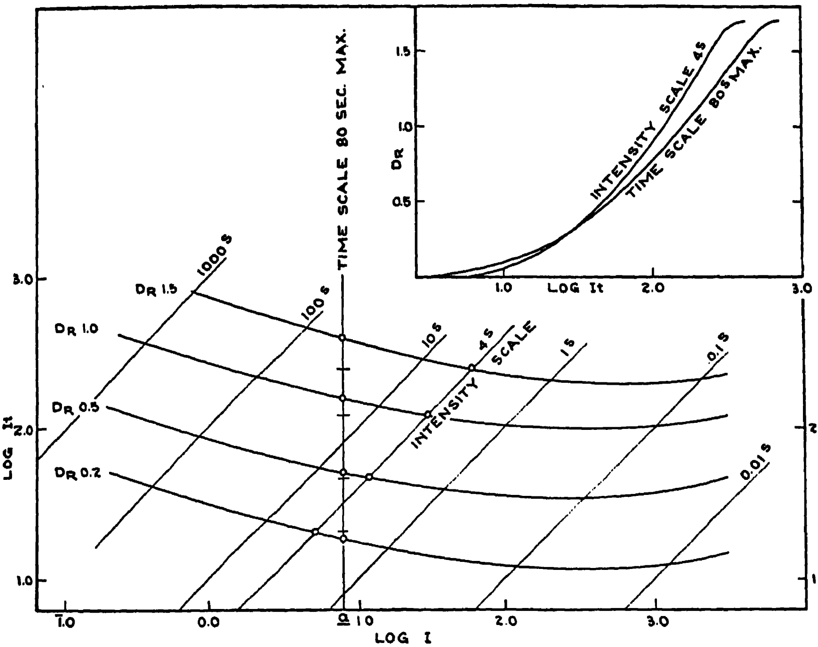


FIG. 169. Reciprocity failure curves for a photographic paper.

Jones and Morrison[30] designed an intensity-scale instrument for the sensitometry of papers which depends upon the use of a cylindrical lens and a stepped diaphragm. A number of such systems have been proposed, and Figure 170 shows the schematic arrangement of several systems represented by Hansen's[31] convention of two orthogonal planes with the respective diagrams of the wedged diaphragm. In all of these, the basic unit is the cylindrical lens *L*. Guilloz[32] in 1909 was the first to apply the principle. He used a continuously wedged diaphragm adjacent to a cylindrical lens, which forms a continuously modulated intensity along a slit (Figure 170*A*). In this simple arrangement, the use of the stepped wedge does not give a sharply defined image of the steps on the image plane unless the source is actually a mathematical line.

Callier[33] in 1910 devised a spectrophotometric condenser (Figure 170*B*) which produces sharply defined steps. The stepped diaphragm is placed next to an evenly illuminated diffusing glass plate *G*. A cylindrical lens *L* images the diaphragm on the exposure plane *E* as a series of modulated steps of equal width. This combination of cylindrical lens and diaphragm became the basis of all later modifications. The system is not efficient in the utilization of the light owing to the diffusing glass. Callier[34] later suggested the use of a cylindrical condenser (Figure 170*C*) in place of the diffusing glass as a means of increasing the efficiency. The condenser would image the source *S* as a strip of light on the lens *L*. This system is also not very efficient.

In an attempt to improve the efficiency of these systems, Miller[35] designed one to modulate the light intensity on the slit of a grating spectrograph (Chapter XVIII, p. 690). He made the condenser lens spherical instead of cylindrical (Figure 170*D*). The image of the source is formed between the cylindrical lens *L* and the slit in one plane and on the slit in the other. A cylindrical field lens at the plane *E* in which the spectrograph slit is placed serves to prevent the loss of light if the system is used with the spectrograph. The diaphragm *D* is placed next to the spherical condenser. The resulting image on the plane *E* consists of a series of sharply defined steps of graded intensities. As with most of the systems of this type, the illuminated area

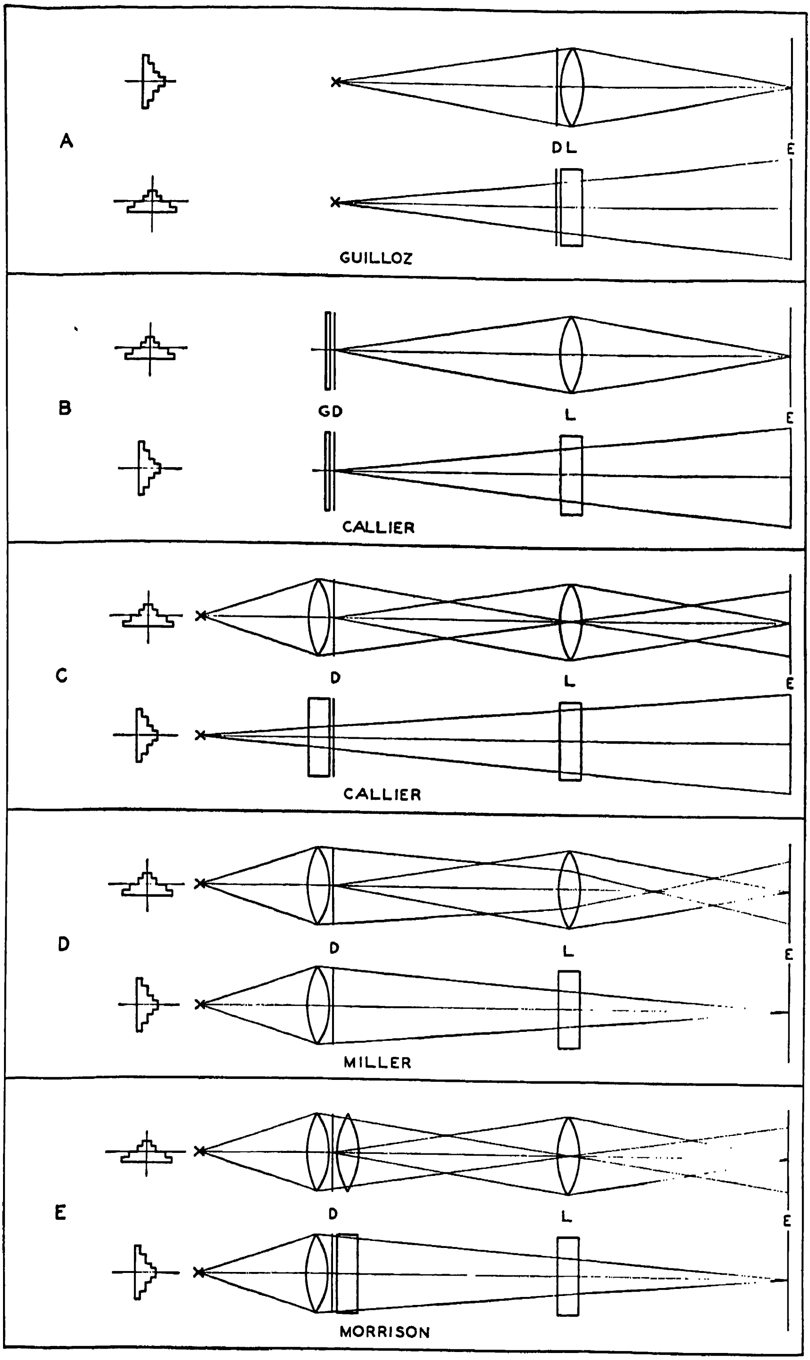


Fig. 170. Optical systems for obtaining graded exposures from a stepped diaphragm.

is still too small and too low in intensity for practical application to sensitometry.

In Morrison's system, shown in Figure 170*E*, the fundamental use of the cylindrical lens to image the diaphragm on the exposure plane is retained. The diaphragm-illuminating condenser consists of a combination of Callier's suggested cylindrical condenser and Miller's spherical condenser. In the instrument designed by Jones and Morrison, this entire optical system and the source of light are mounted on a moving base and traverse the fixed modulating diaphragm and the exposing aperture when the exposure is made. The arrangement is shown in Figure 171, where *P* is a roof prism which translates the motion of the image of the diaphragm into motion in the same direction as the diaphragm. The mechanical design of the instrument is pre-

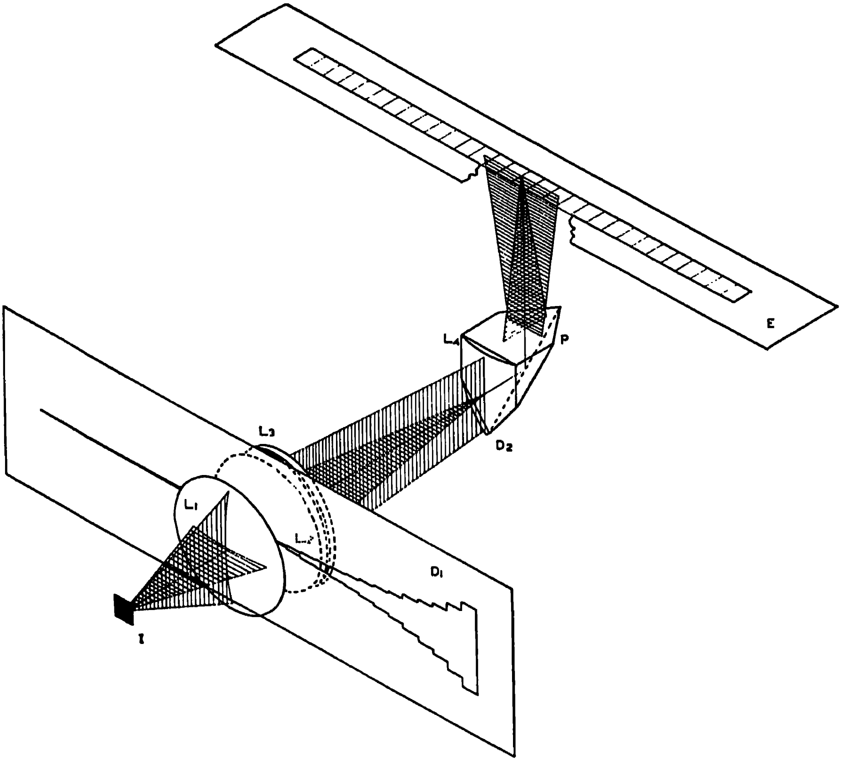


FIG. 171. Optical system of intensity-scale sensitometer.

sented in Figure 172. The shortest exposure time for which this instrument could be used conveniently is about 1/10 second, and the maximum exposure for any given point on the strip, 4 seconds.

A type of sensitometer suitable for general commercial use having an intensity scale has been designed by Tuttle.[48] In this instrument, the use of cylindrical lenses and graduated diaphragms has been abandoned. The instrument depends upon the successive exposure of each step to a uniform field of which the intensity can be controlled mechanically in a known manner. Uniformity is achieved by means of a special illuminating system in which a lamp is placed close to a quartz bar which serves to integrate the light of the lamp so that the ground surface at the end of the bar forms a virtual source of great uniformity. This is imaged on the material by a pair of achromatic lenses, the symmetrical optical system producing a parallel beam of light between the lenses. At this point, there is interposed a series of diaphragms by which the area of the lens used for projecting the light source is graduated, and thus the intensity of the

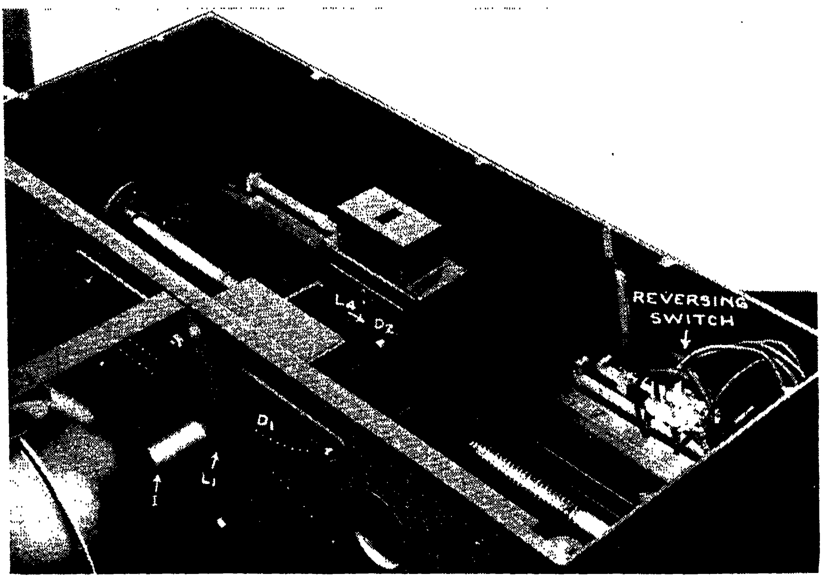


FIG. 172. General view of intensity-scale sensitometer.

incident radiation is graduated without a change in quality. Each step of the material is exposed in turn in the same position, the material holder moving for this purpose; and the diaphragm between the lenses is operated synchronously with the movement of the material. The intensity is so high that exposures of the same level as those used in the camera, *e.g.*, 1/50 second, can be employed; and since the light source and optical train are fixed, the instrument is not unduly expensive to build. It appears likely that intensity-scale sensitometers of this type will replace the older time-scale instruments for all precision sensitometry.

THE CROSSED WEDGE METHOD OF SENSITOMETRY

It seems desirable to describe at this point a simple method introduced by Luther in 1910[36] for obtaining the characteristic curve of a photographic material. This depends upon the use of a graded neutral-tint wedge of square shape. The wedge recommended has a density range from 0 to 6, over 5 inches, giving an intensity range of transmitted light of one million, with a wedge constant of 1.20 per inch. The material to be tested is exposed behind this wedge to a standard light and developed to as high a contrast as possible. The negative is placed over the same wedge, but at right angles to its former position, so that the lines of equal density in the two wedges are at right angles to each other. When the combined negative and wedge are observed by transmitted light, the characteristic curve can be seen as a rather diffused boundary representing a curve of identical density or a curve of points of equal contrast. This curve may be made visible by printing on a suitable material of high contrast, so that a sharp edge can be obtained. The print may have a scale impressed upon it, one of the unit lines being made coincident

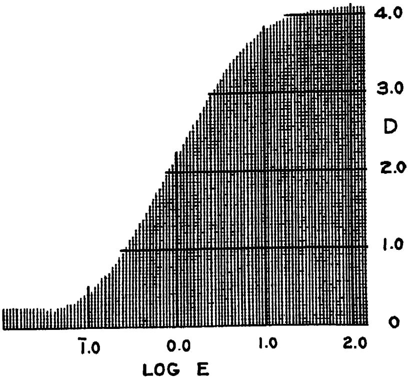


FIG. 173. Print from crossed wedge showing the characteristic curve.

with the position line on the wedge, so that it is of known exposure (Figure 173).

Higson[37] discusses methods of getting sharp edges to the curve, suggesting the use of a chemical reducer and various modifications of the system.

In the negative, the density D_n is a function of the abscissa only, *i.e.*, $D_n = f(x)$, x being the abscissa. In the neutral wedge, the density D_w is proportional to the ordinate, *i.e.*, $D_w = ay$, where a is the wedge constant. On superposition, the resulting density D_k is given by $D_k = D_n + D_w = f(x) + ay$, and the positions of points C, y having the same total density C are given by the equation

$$f(x) + ay = C;$$

hence, as shown by transforming to

$$\begin{aligned} y &= \frac{C}{a} - \frac{1}{a}f(x) \\ &= \frac{C}{a} - \frac{1}{a}D_n, \end{aligned}$$

the ordinates of the curve are proportional to the densities of the negative plus a constant. The multiplying factor, as well as the constant, depends on the wedge-constant and the numerical value of C. The densities, in the vertical direction, are measured from a line of zero density, which is obtained by scraping off gelatin on a straight strip on the edge of the negative alongside the smallest density. The density readings will only agree with visual photometric densities in the absence of any spectral selectivity.

This crossed wedge method of sensitometry has a number of uses. Such applications are described by Watkins,[38] who devised an instrument for measuring γ and for "central speed" determination; that is, by location of the central point of the characteristic curve.

An instrument for the study of gradation and the measurement of γ is described by Renwick; it depends upon the fact that if two crossed wedges are revolved on each other, a position is reached where the slope of the shallower wedge balances that of the steeper. The cosine of the angle of revolution from the crossed position to that of balance, photometrically observed, equals the ratio of steepness of the shallower to that of the steeper wedge. If the wedge constant of the latter is known, γ is obtained from a single measurement.[39]

THE DEVELOPMENT OF SENSITOMETRIC EXPOSURES

It is of great importance in sensitometric work for the test strip to be developed uniformly, since otherwise differences in density due to development will be attributed to exposure. It is very difficult to develop photographic materials uniformly.[40] During development, products are formed which retard development in proportion to their concentration (Chapter XXI, p. 875). Most of them are formed in the most exposed parts, development is retarded more in parts of high exposure than in parts of low exposure, and irregular distribution of the developer therefore produces markings on the material.[34,41] A method of efficient agitation is required to disperse the products of development throughout the whole bulk of liquid as soon as possible after they diffuse from the surface of the film. Mere diffusion or gentle stirring is insufficient; strong, sweeping currents must be produced at the plate surface.

The two most common methods of development are vertical development in a tank and horizontal development in a tray. In vertical development, stirring can be effected either by rotation of the strips in their holders or by external stirring means. The developing tank, being deep, can be completely immersed in a thermostat or surrounded by a water jacket. The vertical rotation of sensitometric strips in glass tubes held in the thermostat was used by Sheppard and Mees and might be expected to be consistent; experiment shows, however, that there is a regular difference of density between the upper and lower portions of the strips and that the advancing half has a higher density than the retreating half. The difference in the vertical direction may be due to the convection effects described by Bullock.[42] He showed that, in most reactions between a photographic material and a solution in which it is held vertically, convection currents are produced by the difference in the specific gravity between the solution containing the products of reaction and the bulk of the solution; these convection currents proceed upward or downward according to the reaction in question. In vertical development without agitation, a downward current prevails, and the degree of development is accordingly greater near the top of the negative. The difference in photographic density due to this cause may amount to 10 per cent.

In a modification of the vertical method of development, the strip may be enclosed in a small jacketed glass tube which may, if desired, be filled completely with developer so as to exclude air. This tube can be shaken by hand, so that agitation is secured by movement of the strip through the developer, the irregular motion giving better results than regular motion by mechanical means. Nietz, who employed the method, compared his results with those obtained from the use of a water-jacketed metal tray and a cylindrical tank fitted with stirrers but was unable to reach any definite conclusions as to which gave the more uniform results. A system adopted tentatively by the British and American Standards Committees for use in the determination of sensitivity employs a vacuum bottle partly filled with developer.[42x] The film sample is attached to a long narrow strip of glass or metal, which is, in turn, fastened to the stopper. Owing to the vacuum jacket, the handling of the bottle during the agitation period produces only a negligible rise in temperature.

Sheppard and Elliott [43] found a considerable effect from the velocity of flow of the developing solution over the gelatin surface. At low rates of flow the velocity of development, as shown by the growth of γ, is little affected by the rate of flow. With developers such as hydroquinone, which are greatly affected by the presence of bromide, weak stirring has an effect similar to that produced by the addition of bromide to the developer. This disappears with adequate stirring. Very high equivalent velocities of stirring are used in motion-picture work; the film passes through tanks containing the developer at speeds as high as 200 feet a minute. Under such conditions, the progress of development is modified substantially from that for a stationary film.

Another method of securing effective flow over the surface of a plate held vertically is that proposed by Dobson and Harrison.[44] They used a plunger which moves up and down in the tank close to the face of the plate. A machine for the automatic development of sensitometric strips was designed by Sheppard and Crouch.[45] This is, in essence, a modification of Harrison and Dobson's tank, with provision for automatic introduction of sensitometric strips at predetermined intervals.

A machine for the development of large numbers of sensitometric strips exposed in the Eastman II-B Sensitometer is described by Jones, Russell, and Beacham [46] (Figures 174 and 175). It accommodates sixty strips positioned vertically on six metal racks, which can be lowered into the developer simultaneously and removed either simultaneously or individually, so that development times may be varied for different parts of the load. The developer circulation across the face of the exposed material is sufficiently rapid that further increase of agitation produces little if any increase in the rate of conversion of latent image into metallic silver. The circulation is of two sorts: (1) a relatively slow, uniform movement of developer in the vertical direction produced by a propeller that forces the developer down into a well external to the main tank, from the lower end of which it spreads out beneath a perforated false bottom in the tank and rises throughout the body of the tank, flowing back again into the top of the well; (2) a much more violent agitation produced by vertical paddles moving back and forth close to the exposed surfaces. Both agitating elements are driven by a synchronous motor, assuring the same rate of circulation. The entire machine is jacketed by thermostatically controlled water. Results show that the circulation throughout the body of the tank is so nearly uniform that they are not influenced by (*a*) whether the heavily exposed end of the sensitometric strip is up or down, (*b*) the position of the strip within the tank, or (*c*) whether a complete or partial load of strips is developed at one time.

While developing machines are of the greatest value for quantity work, it is often desirable to carry out development in a flat tray. Such a tray cannot be immersed in an ordinary thermostat to secure temperature control, but good results can be obtained by using a special water-jacketed tray. A considerable bulk of solution is required, at any rate with developers subject to oxidation, so that the loss of developing agent by oxidation is not serious. If a plate is developed in a flat tray without

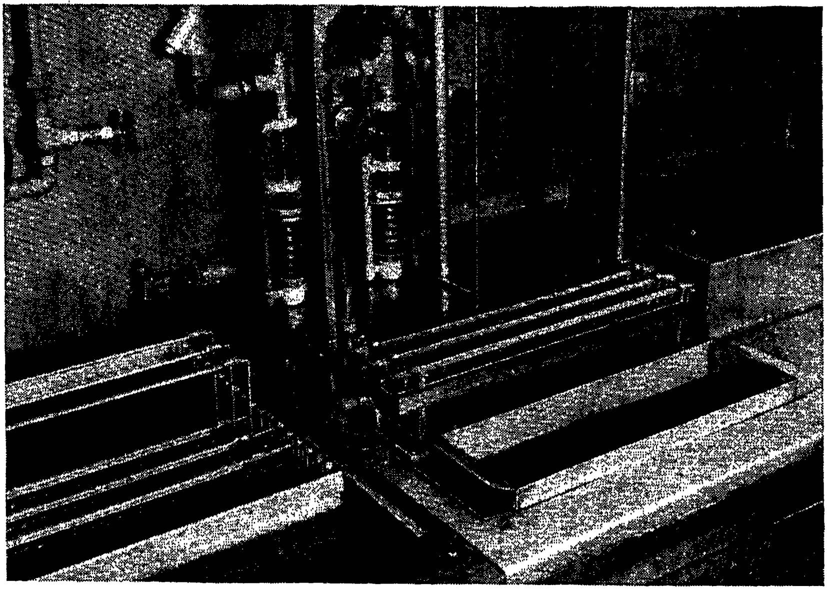


Fig. 174. Developing machine for sensitometric strips.

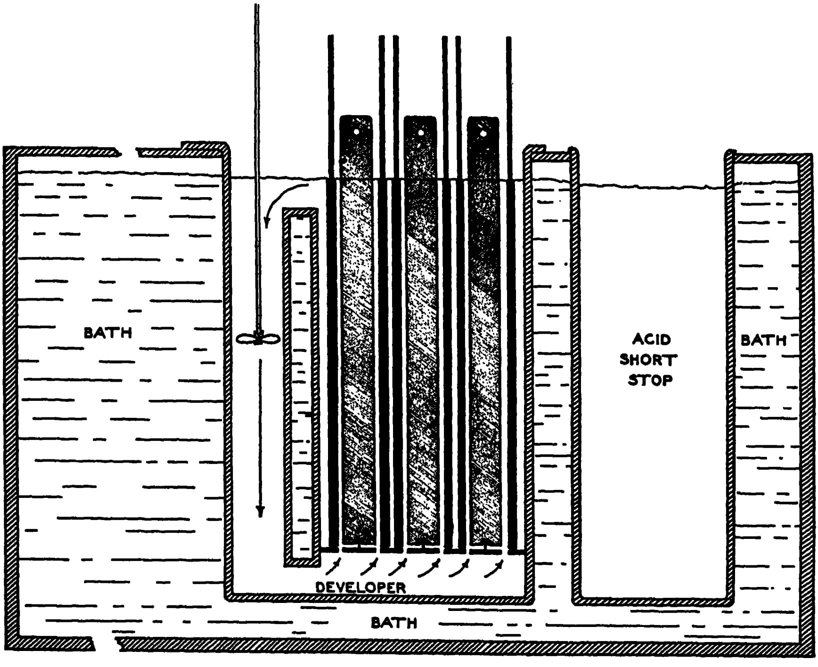


Fig. 175. Section of developing machine.

stirring, areas of even density are often covered with a kind of mottle, due apparently to local concentrations of the products of development. This trouble can be avoided by rocking the tray, but uniform mechanical rocking produces a stationary condition of part of the developer, which results in great differences of density over the plate. By careful, irregular rocking, such a band effect can be avoided, but simple rocking is insufficient to produce the agitation necessary for evenness of development.

Clark,[40] who studied the evenness of development at length, recommends that the strips be brushed continuously during development with a soft, flat, long-haired brush. The right type of brush does no damage to the emulsion, and broad brushes to cover three or four inches of strip can be employed. This gives very uniform development, and the only objection seems to be that brushing increases the rate of development, as would be expected, by removal of the products of development and that this increase depends upon the exact method of brushing, so that it is rather difficult to repeat the results.

A comparison between the use of the brush and the developing machine was made by Jones, Russell, and Beacham, with three different workers using brush development. The variation in density for the same exposure was found to average 0.11 for the brush-developed strips compared with 0.03 for the machine. For reproducibility, therefore, the machine is greatly superior to the use of the brush. On the other hand, if uniformity over a considerable surface is of prime importance, it is probable that the brush method is as good as any.

DEVELOPERS FOR SENSITOMETRIC WORK

The choice of a suitable developing solution for sensitometric work has received much attention. Frequently, the purpose of sensitometry is to determine the properties of the material—for example, its effective speed—for use in practical photography. In this case, the development should be identical with that used in practice. Not only should the same composition of developer be used, but the temperature, agitation, and replenishment of the solution should be those which obtain in practical work. As a general rule, therefore, the developing solutions used in sensitometry are not those most suitable for use in investigations of the principles of photography but those which are used in practice for the development of the materials studied. In the earlier experimental work, standard developers of a type which could be controlled conveniently by chemical analysis were generally adopted.

Driffield[47] in a paper summarizing the results of the photochemical investigations made by himself and Hurter writes:

> "As the result of our earlier investigations we decided in favor of ferrous oxalate as our standard developer, and an excellent standard it is from many points of view. It has, however, never been a popular developer and it has the drawback of being considerably less energetic than alkaline pyrogallol. After further investigation, therefore, we decided to employ a pyro-soda developer as our standard, satisfying ourselves that it possessed the requisite qualifications."

The ferrous oxalate developer used by Hurter and Driffield has the following composition:

A	*Parts*	*C*	*Parts*
Potassium Oxalate	1	Potassium Bromide	1
Water	4	Water	100
B		*For use take:*	
Ferrous Sulfate	1	*A*	100
Citric Acid	0.01	*B*	25
Water	3	*C*	10

Development to be conducted at a temperature of 65° F.

Mees and Sheppard also used a ferrous oxalate developer and considered it a possible standard for sensitometric measurements but discarded it later as unsuitable. While all its constituents are inorganic compounds easily procurable in a high state of purity and susceptible of precise analysis by relatively simple chemical methods, its unsuitability for practical use makes it undesirable for use in the sensitometry of commercial materials.

The standard pyrogallol formula adopted by Hurter and Driffield in 1898 is as follows:

	Parts
Pyrogallol	8
Sodium Carbonate (recrystallized)	40
Sodium Sulfite (")	40
Water to make	1000

It should be noted that the pyrogallol formula contains no bromide. Driffield[47b] says, "This omission is of the utmost importance, and must be insisted upon, at any rate, when determining the speed of a plate. While the pyrogallol and the alkali are essential elements of the developer, a bromide is altogether unessential."

For many years a pyro developer was used very extensively in practice and, while no official standard was ever adopted for sensitometry, a pyro formula was used almost exclusively in production control, research, and practical sensitometry. While it is true, as stated by Hurter and Driffield, that bromide is an undesirable constituent of a developer since it makes the value of the inertia dependent upon the time of development, nevertheless the presence of a small amount of bromide is desirable from the practical point of view to prevent an excessive increase in fog if development time is greatly prolonged. The following formula was used for many years in a large laboratory and found very satisfactory for most sensitometric work.

Solution A	
Sodium Sulfite (anhydrous)	70 gm.
Sodium Bisulfite (anhydrous)	17 gm.
Pyrogallol	20 gm.
Water to make	1,000 cc.
Solution B	
Sodium Carbonate (anhydrous)	75 gm.
Potassium Bromide	1 gm.
Water to make	1,000 cc.

For use, take equal parts of *A* and *B*.

During recent years, pyrogallol has been used less and less in practical work, not at all in motion-picture processing, and to a negligible extent in the development of amateur negatives. It appears, therefore, to have ceased to meet the needs for standardized sensitometry. The question of an international standard developer for sensitometry was discussed at the Sixth International Congress of Photography.[49] The pyro standard was considered and rejected. The proposal for a metol-hydroquinone formula made by Odencrants also was objected to largely on the ground that it seemed undesirable to adopt a formula having two reducing agents. Sheppard proposed a *p*-aminophenol formula which met with considerable favor. In a paper by Sheppard and Trivelli,[50] read at the Seventh International Congress of Photography, the characteristics of this reducing agent and its adaptability to a standard formula were discussed, the following formula being recommended:

p-Aminophenol Hydrochloride	7.25 gm.
Sodium Sulfite (anhydrous)	50.00 gm.
Sodium Carbonate (anhydrous)	50.00 gm.
Water to make	1000.00 cc.

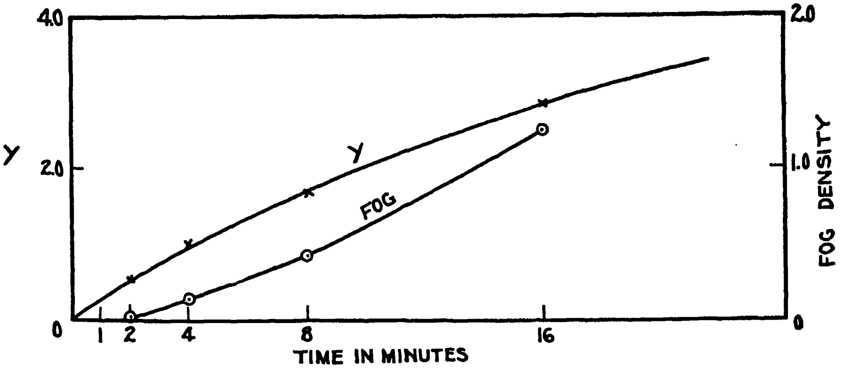
It should be noted that this formula contains no bromide and, therefore, unless there should be free bromide present in the photographic material itself, there should be no regression of the inertia with increase in time of development, and speed should be independent of development time. Moreover, this developer is relatively insensitive to the presence of bromide; and hence, even if free bromide is present in the photographic material, the effect upon value of inertia should be relatively small. In Table LXV are given the speed values obtained with this standard developer compared with those obtained with pyrogallol and with a metol-hydroquinone formula for two widely different types of photographic materials. In both cases, the speed value for the proposed standard lies between those given by the other two reducing agents.

TABLE LXV

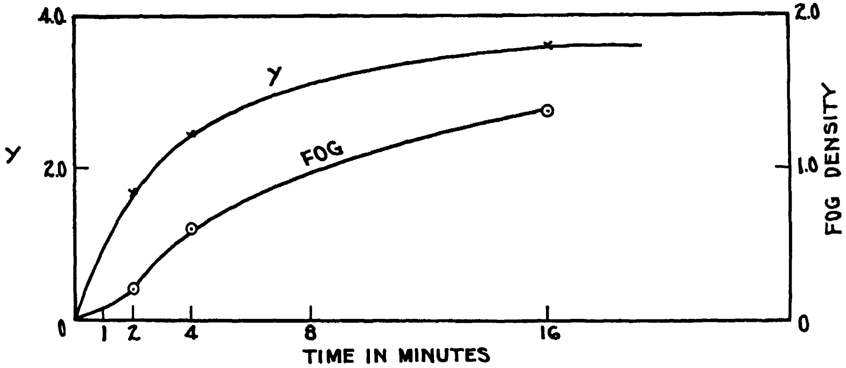
Relative Speed Values Obtained with Developer Formulas

Low-Speed Material	
p-Aminophenol	21.4
Pyrogallol	25.1
Metol-hydroquinone	19.9
Medium-Speed Material	
p-Aminophenol	63.2
Pyrogallol	60.1
Metol-hydroquinone	65.2

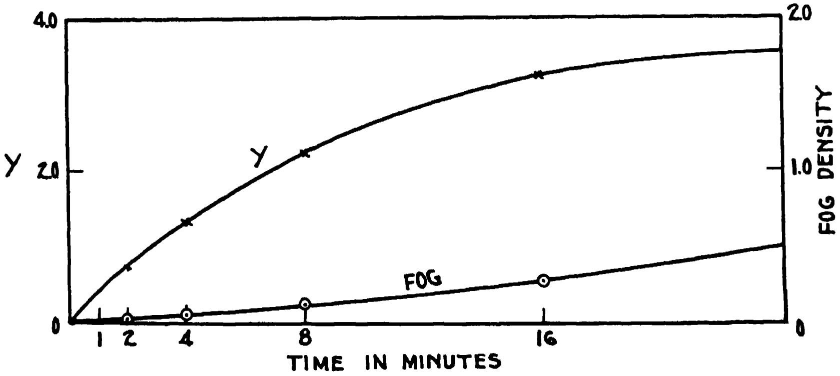
Curves showing the growth of γ and of fog with the time of development for the three developers are shown in Figure 176. The *p*-aminophenol formula shows excellent behavior from the standpoint of fog characteristics. It gives a gray (non-selectively absorbing) deposit; therefore, readings of density made visually correspond to the effective photographic density values.



γ, *t*, and fog curves for metol-hydroquinone



γ, *t*, and fog curves for pyrogallol



γ, *t*, and fog curves for *p*-aminophenol

FIG. 176.

At the Eighth International Congress of Photography, this developer was adopted as the standard for scientific sensitometric work.[51]

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CHAPTER XVII

THE MEASUREMENT OF DENSITY

A statement of the amount of the photographic image produced by exposure and development may be in terms of (*a*) the mass of silver per unit area or (*b*) the absorption of light by the material. The first is of value in considering the chemical reactions involved, while the second applies directly to the use of the image in photography; *e.g.*, in relation to the tone reproduction.

Since the analytical determination of the mass of silver is laborious, it is undertaken only to determine the relation between the mass of the image and its optical properties, and in practice the measurement of the image is accomplished by a determination of the absorption of light.

Hurter and Driffield defined the *density* of a photographic deposit as follows:

> "The intensity I_x of light after passing A molecules of a substance is a fraction of the original intensity I, such that
>
> $$\frac{I_x}{I} = \left(\frac{1}{C}\right)^A.$$
>
> For purely mathematical reasons the fraction $\frac{1}{C}$ is usually expressed as a negative power of the base of the hyperbolic logarithms e, say $\frac{1}{C} = e^{-k}$, and we can write
>
> $$\frac{I_x}{I} = e^{-kA},$$
>
> where k is called the coefficient of absorption. This form of the law we shall frequently use again. The fraction $\frac{I_x}{I}$ represents and measures the *transparency* of the substance. The inverse of that fraction, or
>
> $$\frac{I}{I_x} = e^{kA},$$
>
> measures the *opacity* of the substance. It indicates what intensity

of light must fall on one side of the substance in order that unit intensity may be transmitted.

"In our investigations we use the letter T to denote transparency, and O to denote opacity, and the two symbols are related thus:

$$O \times T = 1.$$

"We must further define what we mean by density as distinct from opacity. By density we mean the number of particles of a substance spread over unit area, multiplied by the coefficient of absorption; $k \cdot A$ is what we term density, and mark by the letter D.

"For our purposes, *i.e.*, in its application to negatives, the density is directly proportional to the amount of silver deposited per unit area, and may be used as a measure of that amount.

"The relations between the three terms, transparency, opacity and density, are the following:

$$T = e^{-D},$$
$$O = e^{D},$$
$$D = \log_{.e} O = -\log_{.e} T.$$

"The density is the logarithm of the opacity, or the negative logarithm of the transparency.

"These relations hold good for some substances with regard to ordinary white light, for others only with regard to monochromatic light, and for others they do not hold good at all. We have satisfied ourselves that they do hold good for the silver deposited as a black substance in negatives so long as the silver does not assume a metallic lustre, and reflects but a very small amount of light."

In practice, however, Hurter and Driffield used the relation

$$D = \log_{10} O = -\log_{10} T.$$

Their conclusion that the density was proportional to the mass of silver per unit area was confirmed by subsequent workers, but later studies have shown considerable departures from proportionality. This matter is discussed elsewhere (Chapter V, p. 226).

The measurement of the density is made with some form of photometer which compares the light transmitted by the density with that incident upon it. A photographic image, however, is not completely transparent; it is rather translucent, scattering an appreciable portion of the light falling upon it. The amount of the transmitted light as read in the photometer depends consequently upon the proportion of the scattered light collected in the photometer. This is illustrated by Figure 177; a beam of light is incident upon the silver image shown at *A*, and the distribution of the transmitted light is indicated by the shape of the figure *MNP*. A large proportion of the light is transmitted in the direction *N*; but much of it is scattered, as indicated at *M* and *P*. As a result, the value of the density of the silver deposit varies according to the type of photometer. Thus, a photometer at *N* receives only the light transmitted through the narrow angle, and the scattered light is counted as absorbed by the deposit. On the other hand, if a photometer is used which receives all the light emerging from the layer *A* and integrates it for measurement, the value of density found will be considerably lower than in the first case. A method of making these measurements is shown in Figure 178. An integrating sphere, *S*, is used, to which is attached the photometer, *O*, the observer looking into the sphere through a hole in its side at an area on the opposite wall. If the sphere is at a considerable distance from the absorbing density *D*, as shown in *A* of the figure, the directly transmitted light is measured; and the value of density includes the loss of the scattered light which does not enter the sphere. This is termed the *specular density*. On the other hand, in *B*, the integrating sphere is in contact with the density to be measured. All the light transmitted by the density, including all the scattered light, enters the sphere; and a lower value of the density is obtained, which is referred to as the *diffuse density*.*

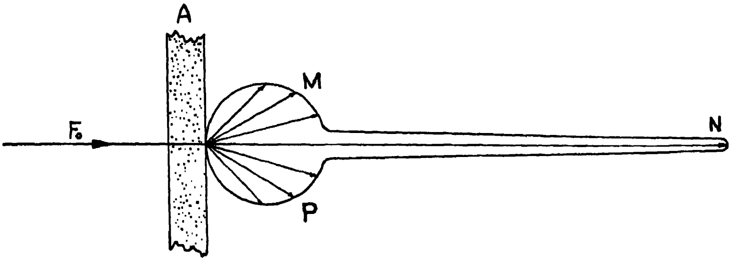

FIG. 177. The transmission of light through a photographic image.

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* In order that the sphere may act properly as an integrating photometer, the observed spot, *S*, should be screened from direct light from the source. It should be illuminated only by light reflected one or more times by the sphere wall; therefore, in *B* of Figure 178, an opaque screen, *M*, intercepts light scattered by the sample in the direction of *S*.

The effect of scattered light upon the value of density readings caused some disagreement between Hurter and Driffield and their critics.[1] Hurter and Driffield's photometer measured approximately specular densities, because the photometer head was at a considerable distance from the density to be measured and in the path of a more or less parallel beam of light from an oil lamp. Abney measured his transparencies by placing the density in contact with a scattering medium, such as a piece of translucent paper or opal glass, so that the scattering of light by the silver affected the density reading less in Abney's instrument than in that used by Hurter and Driffield. Abney correctly ascribed the difference to the light-scattering property of the silver deposit, while Hurter and Driffield thought that it was due to interreflections between Abney's diffusing medium and the negative. The matter was cleared up in 1898 by Chapman

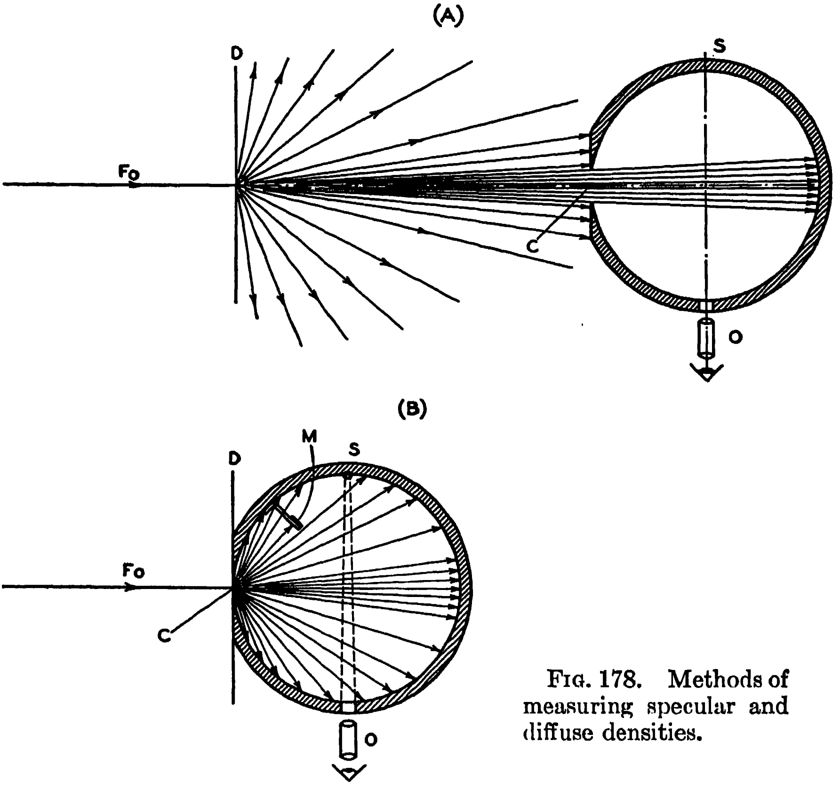

Fig. 178. Methods of measuring specular and diffuse densities.

Jones,[2] who confirmed Abney's idea that, under the conditions used by Hurter and Driffield, there was a loss of light by scattering which resulted in a higher value of the density than that obtained if the negative was illuminated by diffused light.

In 1909, Callier [3] made a large number of measurements to determine quantitatively the relation between the specular density, which he referred to as *D//*, and the diffuse density, which he referred to as *D#*. The ratio of *D//* to *D#* he designated as *Q*, and since that time this ratio has usually been referred to as *Callier's Q factor*. He found that *Q* is constant for all values of density, and a single number therefore represents the relation between specular and diffuse density values for a given material. In Table LXVI are shown some typical values of the *Q* factor for various photographic materials.

TABLE LXVI

RATIO OF SPECULAR TO DIFFUSE DENSITY (*Q*) FOR VARIOUS TYPES OF PHOTOGRAPHIC MATERIALS

Material	*Q Value*
Lippmann plates (grainless)	1.0
Very fine-grained transparency plates	1.2
Lantern plates	1.35–1.5
Medium-speed plates	1.6
High-speed plates	1.7
Highest-speed plates intensified with mercury	1.9

The Callier coefficient obviously is related to the graininess of the deposit. Thus, the Lippmann plates, which are essentially grainless, have a *Q* value of unity; and the value of *Q* increases with the graininess of the material. Threadgold suggested that the value of *Q* could be used as a measurement of the graininess of the deposit, and the matter was studied experimentally by Küster and by Eggert and Küster. For an account of their work, see Chapter XXI, p. 849.

The relation between diffuse and specular density was investigated by Renwick and Bloch,[4] who found that *Q* is not constant for all values of density but can be expressed as a logarithmic function of density, so that if the logarithm of the diffuse density is plotted against the logarithm of the specular density, straight lines are obtained. Tuttle[5] studied the subject experimentally and verified the findings of Renwick and Bloch.

Experiments made in the Kodak Research Laboratories* show that Q varies not only with density but with γ. In Figure 179, the values of Q found for the densities of sensitometric strips of motion-picture positive film are plotted against the diffuse densities. It is seen that the value of Q depends directly upon the γ to which the strip was developed. In the same strip, the value depends upon the density and, after passing through a maximum at diffuse densities approximating 0.3, decreases somewhat as the density increases. For very low densities, the value of Q is low. To obtain such low values of Q experimentally, the greatest care is necessary to eliminate dirt, scratches, and other extraneous sources of scattered light.

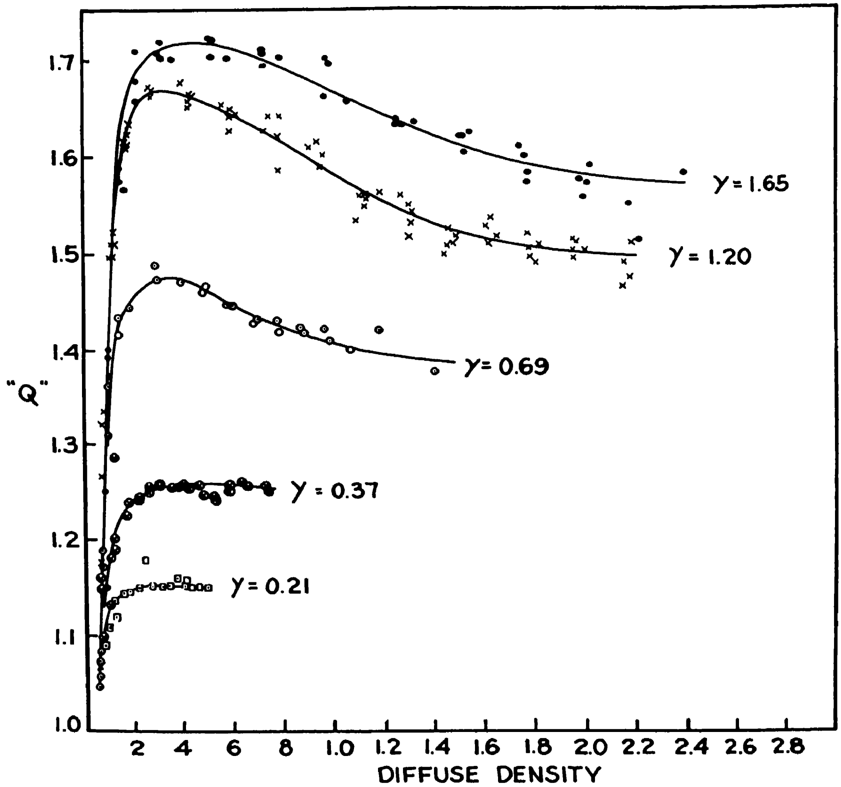

FIG. 179. Curves showing the relation between Q, γ, and the diffuse density.

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* O. Sandvik, private communication.

As a means of evaluating scattered light, Bull and Cartwright[6] suggested the use of two integrating spheres in series, the first one having diametrically opposed apertures so arranged that a parallel beam of light would pass through to the second sphere without illuminating the first. If a density was placed over the window of the first sphere, this sphere was illuminated only by scattered light, while the second sphere, according to the authors, measured "the photographic density in parallel light." In their arrangement, the first sphere, illuminated by scattered light, must have served as a partial light source for the second sphere, and the density value would consequently be somewhat lowered.

In the strictest sense, the value of specular density cannot be determined directly. The photometric receiving element, even though it is positioned so as to receive only rays of light normally and quasi-normally transmitted by the sample, collects those rays which are scattered in the normal or quasi-normal direction as well as those which are directly transmitted.

Silberstein and Tuttle[7] analyzed the problem and derived a formula relating the specular and diffuse densities as follows:

$$10^{-D/\!/} = E \cdot 10^{-D/\!/} + (1 - \epsilon) \cdot 10^{\beta D\#}$$

where ϵ is a constant expressing the fraction of the scattered light which emerges normally or quasi-normally; *i.e.*, the amount accepted by the photometric field of a densitometer or by the projection lens of such a device as an enlarging printer. The constant β = unity plus the ratio of scattering to absorption coefficients. The smaller the value of ϵ, the more nearly will the density approach strict proportionality, as stated by Callier. If $\epsilon = 0$, β is numerically equal to Callier's Q. If $\epsilon = 1.0$, $D/\!/ = D\#$.

Pitt[8] outlined an experimental procedure that yields data from which the true specular density may be calculated. He found that the ratio of the scattered light in the normally transmitted beam to the light in the undeviated portion of the beam increases linearly with density.

Optical effects other than those attributable to scatter influence the numerical value of a photographic density whether it is used in a printer or measured in a densitometer. Toy[9] pointed out that in contact printing the optical factors influential in determination of the effective density of a negative are:

1. Interreflection between printing medium and negative,
2. Color of the printing light,
3. Parallelism of the printing light.

The results of previous work on the direct determination of effective printing density had been vitiated by reciprocity law failure, and Toy's experiments were carefully worked out to avoid error from this cause. He formulated a definition of printing density, as follows:

> "The printing density of a negative is the common logarithm of the number representing the intensity which will produce, through the negative in contact with a printing medium, the same effect on the print as unit intensity will produce through the glass only for the same time of exposure and conditions of development."

Toy terms this value $D\phi$; but the symbol D_p, used by Jones, would seem to be preferable. Toy concludes that the readings of a densitometer in which the density was placed in contact with opal glass could be converted to printing density values by a simple factor. Renwick[10] disagrees with this general conclusion; he states that a specular density reading is a better reference standard.

Toy[11] found that in an extreme case the interreflection effect might account for an effective density change of 0.03 but points out that the predictable *variation* in printing density resulting from differences in reflectance of the positive material would be of the order of 0.02. The lowest effective contact-printing density would correspond to the higher negative and positive reflectance. Renwick[12] disagrees with Toy's analysis and cites evidence indicating that the interreflection effect could be greater than Toy expected.

Toy found in investigating the effect of the color of the incident light, which he did by varying the voltage applied to the printing lamp, that only a small variation of printing density accompanied a large change in color of the source. He made no observations upon one factor important in contact printing; namely, the effect of the direction of the incident light. That it is not a negligible factor can be inferred from analyses made by Selwyn and Pitt[13] and Koerner and Tuttle.[14] For a layer of given absorption per unit path length, the effective density depends upon the length of the path through the material. Thus, if the density of a layer for a ray incident and transmitted normally is D_0, its density for a ray incident at angle θ will be given by $D_\theta = \frac{D_0 n}{\sqrt{n^2 - \sin^2\theta}}$, where n is the refractive index of the material. If, then, a positive material is placed in contact with a negative illuminated by diffuse light, the average path traversed by rays of light before reaching the positive will be longer than would be the case for normal illumination by collimated light, and the effective density of the negative will be increased. The contrast of the contact print made by diffuse light will be slightly higher than that of a print made by collimated light—exactly the reverse of the Callier Q effect, which applies to projection printing by collimated or diffuse light.

Density is obviously not a simple, invariable property of a photographic deposit, and the safest rule for its accurate evaluation is to measure the light-stopping power of each sample in the way in which it is used. Application of this rule is impractical, and many of the references in this chapter deal with the search for methods of mathematical conversion from one densitometer reading to one photographic application. Tuttle and Koerner, for instance, have done this systematically for a variety of so-called *diffuse density* measuring instruments and effective contact-printing results.

There is a considerable need for an internationally standard method for the determination of density. The recommendation was made at the Eighth International Photographic Congress[15] that photographic density be defined as the logarithm of the ratio between the brightness of the upper surface of an opal disk uncovered and that of the surface covered with the density to be measured; the density to be placed in contact with the opal and the measurement made in a direction perpendicular to its surface; the opal disk to be of such a thickness that the measured value does not alter if a thicker opal is used.

Davies and Owen,[16] realizing the effect of interreflection, proposed to eliminate the opal reflection influence by referring the measurement to the opal covered by a piece of the base. Later, Selwyn and Pitt[12] suggested reversal of the position of opal and density—the opal to be between the density and the measured element. This arrangement avoids errors caused by the effect of the density sample upon the distribution of light entering the photometer.

Tuttle and Koerner,[17] feeling that the integrating sphere is more reproducible to specification and freer from reflectance variation difficulties than a piece of opal glass, recommended this device as a standard for diffuse density measurements. The Standards Committee of the Society of Motion Picture Engineers acted favorably on this suggestion and adopted it as recommended practice.[18]

THE SPECTRAL SELECTIVITY OF PHOTOGRAPHIC DEPOSITS

Another factor of importance in connection with the printing value of photographic densities is their color (Chapter XIV, p. 555). In general, a colored photographic image gives a characteristic curve having almost the same inertia as the visual curve but a different value of γ (Figure 180). The effect of the color can obviously be stated as *the ratio of the photographic to the visual* γ, with the understanding that the photographic γ is determined on a specific printing material printed by a specific light source.

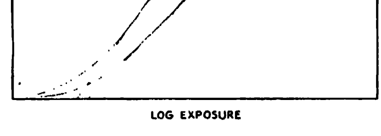

FIG. 180. Characteristic curves showing the photographic and visual densities of colored images.

Jones and Wilsey[19] considered at length the spectral selectivity of different photographic images. Choosing as the printing material bromide paper printed with a light source of 2360° K., they termed $\frac{\gamma_p}{\gamma_v}$ the color coefficient χ. For negatives developed with the so-called *nonstaining* developers—such as ferrous oxalate and hydroquinone—the value of χ is low, usually below 1.1. If pyrogallol is used as the developer, however, the negative has a more or less yellowish color, according to the amount of sulfite used in the developer, the yellow color being due to an oxidation complex of the pyrogallol deposited with the silver (Ch. X, p. 392). It is possible to show this very clearly by removing the silver and leaving an image consisting of the yellow oxidation product only. The yellow image is largely removed by fixation in an acid fixing bath, but if the negatives are fixed in a plain hypo solution, very high values of χ may be obtained. For a pyro developer containing 50 grams of pyro per liter, 10 grams of sodium carbonate, and sodium sulfite ranging from 0 to 50 grams per liter, the color coefficient varies as follows:

TABLE LXVII

Sulfite	*Color Coefficient*
50	1.16
25	1.24
15	1.30
10	1.45
5	1.80
0	2.75

A negative developed with 50 grams of sulfite per liter is therefore quite gray and prints with little more strength than appears to the eye. Portrait negatives developed with pyrogallol are usually made to have a color index between 1.3 and 1.50, 10–15 grams of sulfite per liter being used. If the sulfite is omitted, the printing density is almost three times the visual density.

In intensified images, the color is often far from neutral, and the color coefficient of such images is of great importance in relation to the degree of intensification obtained by any treatment.[20] Wilsey, indeed, proposed the use of pyro-developed images as a means of intensification and reduction[21] (Chapter XIV, p. 555).

A photographic image on a material of very fine grain shows selective absorption as a result of its selective scattering of light (Chapter XV). The introduction of fine-grain films for making motion-picture sound negatives has made it necessary to correct the visual density measurements of these negatives for the color coefficient to obtain the effective printing density. Frayne[22] has applied the integrating sphere densitometer (p. 663) to these measurements, by equipping it with a special photosensitive cell and color filter, to obtain a spectral range close to that of positive motion-picture film. He finds that the color coefficient of the fine-grain materials is a function of the negative density and, therefore, that the color of the image must be attributed, in part at least, to light scattering by the grains rather than to a developer stain.

THE CORRECTION OF DENSITY READINGS FOR FOG

Fog is the term used to designate the density produced in development which is not due to the exposure to light (Chapter XI, p. 450). The densities read from sensitometric strips do not require fog correction if the densities are to be used in tone reproduction analyses. The printing characteristics of a negative are related to the total densities occurring in the negative regardless of how these densities were produced. For many purposes, however, it is necessary to correct the density readings for the presence of fog. Hurter and Driffield measured the fog density on unexposed portions of the plate and deducted the value found from all observed densities. They recognized the fact that the fog was not distributed uniformly over all image densities; it must be expected to be greater upon an unexposed portion of the plate than where considerable exposure and development had occurred.

Meidinger[23] calculated a correction for the decrease in fog with increased image density. He assumed that the fog over the image is proportional to the number of grains of silver halide not developed as exposed grains. In the terminology adopted by Wilsey,[24] if D_f is the fog deduction, D_m the maximum density obtainable by any exposure and development, D the observed density, and F the fog density on unexposed areas,

$$D_f = aF$$

where

$$a = \frac{D_m - D}{D_m - F};$$

that is,

$$D_f = \left(\frac{D_m - D}{D_m - F}\right)F.$$

Since the deduction for fog is assumed to be proportional to the number of grains not developed, unless development is carried to completion, some of the grains deducted as fog are exposed.

Wilsey therefore suggests a modification in which the fog over the image is assumed to be proportional to the mass of the silver unaffected by exposure. Then,

$$D_f = \left(\frac{D_m - D_\infty}{D_m}\right)F,$$

where D_∞ is the limiting image density obtainable by continued development of the exposure considered. If F is measured on an unexposed area remote from the density, its value will be higher than if the area under consideration were exposed to the products of reaction effective in the exposed area. It is, of course, impossible to obtain an unexposed area in which the grains are developed exactly as if they were in an exposed area; but an approximation to this was suggested by Bloch,[25] who recommends that small unexposed areas be left in the middle of exposed areas, so that the development conditions are approximately the same. It is possible also that the susceptibility to exposure of grains subject to fog may be different from that of the grains which are not likely to fog.[26]

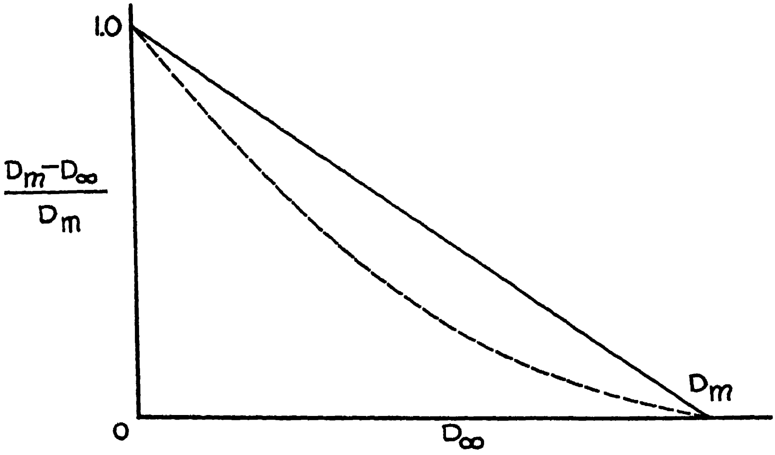

FIG. 181. The relation between D_∞ and $\frac{D_m - D_\infty}{D_m}$.

The matter was studied at some length by Pritchard,[27] who worked out experimental methods of correcting for fog from a study of the growth of fog after the image density is almost completely developed. He points out that the correcting factor $\frac{D_m - D_\infty}{D_m}$ in the Wilsey formula is a straight-line function of the completely developed image density D_∞. The solid line in Figure 181 shows this relation. The end-points of this line are correct, that is, at zero exposure the full observed fog value F is to be deducted, and when maximum density, representing all the developable silver in the film, is reached, there should be no deduction for fog. If exposure has a selective action on fog grains, the fog over the image usually would be less than that computed by the Wilsey formula, and the curve for the fraction should lie below the straight line of Figure 181 but have the same end-points.

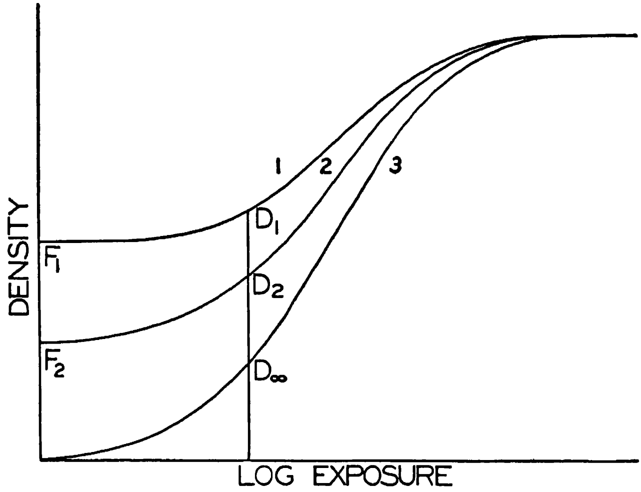

FIG. 182. Application of the correction for fog to the characteristic curve.

Variations in the photometric equivalent (page 226) could produce a similar effect. Thus, the true fog correction function may be similar to the dotted curve. This type of relation was found experimentally by Nietz. His data give for the first part of the curve a straight line intersecting the density axis at a value less than D_m. The values of the fog correction factor D_f were derived from sensitometric curves for long development times by the following method: In Figure 182 let curve 1 represent a characteristic curve in which both fog and image have been developed to completion; curve 3 is a hypothetical curve for image density alone, the D_∞, $\log E$ curve. In correcting any density, D_1, to give the true image density, D_∞, a fog density equal to $D_1 - D_\infty$ must be subtracted. Thus $D_f = D_1 - D_\infty$; $D_f = \frac{(D_1 - D_\infty)F_1}{F_1} = \alpha F_1$. Consider the experimental curve 2 in which it is assumed that the image is completely developed but fog is not. If all fog densities increase in the same proportion as development proceeds, regardless of the image densities with which they are associated, the differences between the three curves will be in direct proportion. Thus, $(D_1 - D_\infty)/F_1 = (D_2 - D_\infty)/F_2 = (D_1 - D_2)/(F_1 - F_2) = \alpha$; α is seen in this case to depend upon the difference in density between two curves for times sufficient to develop the image completely.

The method for finding the fog correction is as follows: Strips are developed for a time sufficient to develop the image approximately to completion; *e.g.*, thirty to sixty minutes. The density values are now corrected by the use of Meidinger's formula, so that a first approximation to D_∞ is obtained as $D_\infty = D_1 - \alpha F$, where D_1 is the density obtained and

$$\alpha = \frac{D_m - D_1}{D_m - F}.$$

Thus, a first approximation curve can be obtained by plotting the values calculated for D_∞ against $\log E$. Then, using a $\log E$ which gives a value of D_∞ close to the shoulder of the curve but still on the straight line, Wilsey's formula,

$$D_f = F \cdot \frac{(D_m - D_\infty)}{D_m},$$

is used to find the correction to be applied to each curve at the $\log E$ chosen.

A second approximation to D_∞ at this same $\log E$ can be found by Nietz' method, which utilizes the principle that $\log \frac{D_\infty}{D_\infty - D_1}$ plotted against the logarithm of the development time gives a straight line for the proper D_∞. By trial and error, then, a corrected D_∞ is determined. The corrected D_∞, $\log E$ curve is drawn through this new value of D_∞, with the new D_∞'s at the other log E's plotted as much larger than their first approximations as the calculated D_∞ increased over its first approximation.

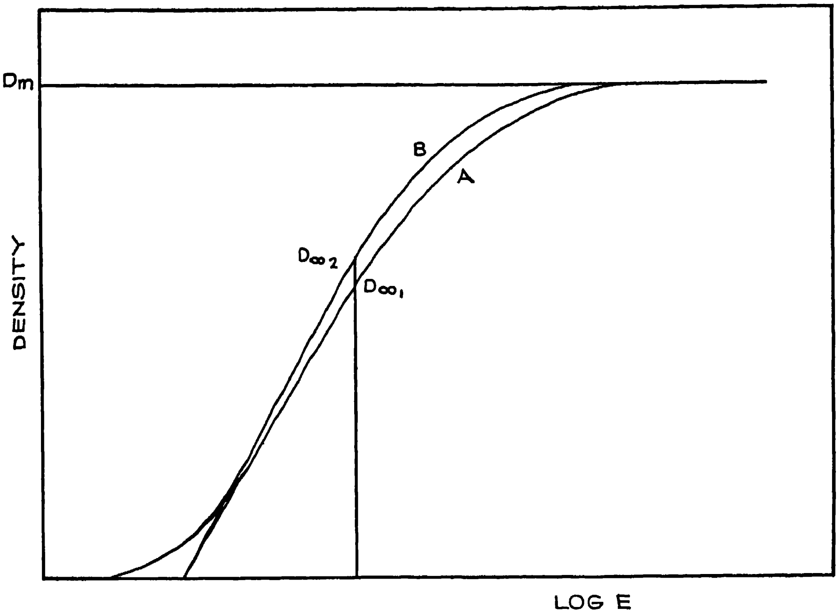

FIG. 183. First and second approximations to the D_∞, log E curves.

Straight-forward calculations by Wilsey's formula will now yield the corrections to be applied. The first and second approximations to the D_∞, log E curves are shown in Figure 183.

DENSITOMETERS

The instruments used for the measurement of photographic densities are often called *photometers*, but it is better to retain the term photometer for an instrument which measures the intensity of light and to refer to instruments measuring photographic absorption as *densitometers*.

Many methods and instruments have been devised for measuring the density of the silver deposit. Hurter and Driffield used a modified form of the bench photometer, such as that employed for making intensity measurements in photometric laboratories. In such an instrument, two light sources are used, both of which must be kept at constant intensity while the measurements are being made. The photometer head, in which the intensity balance is made, may be any one of several types

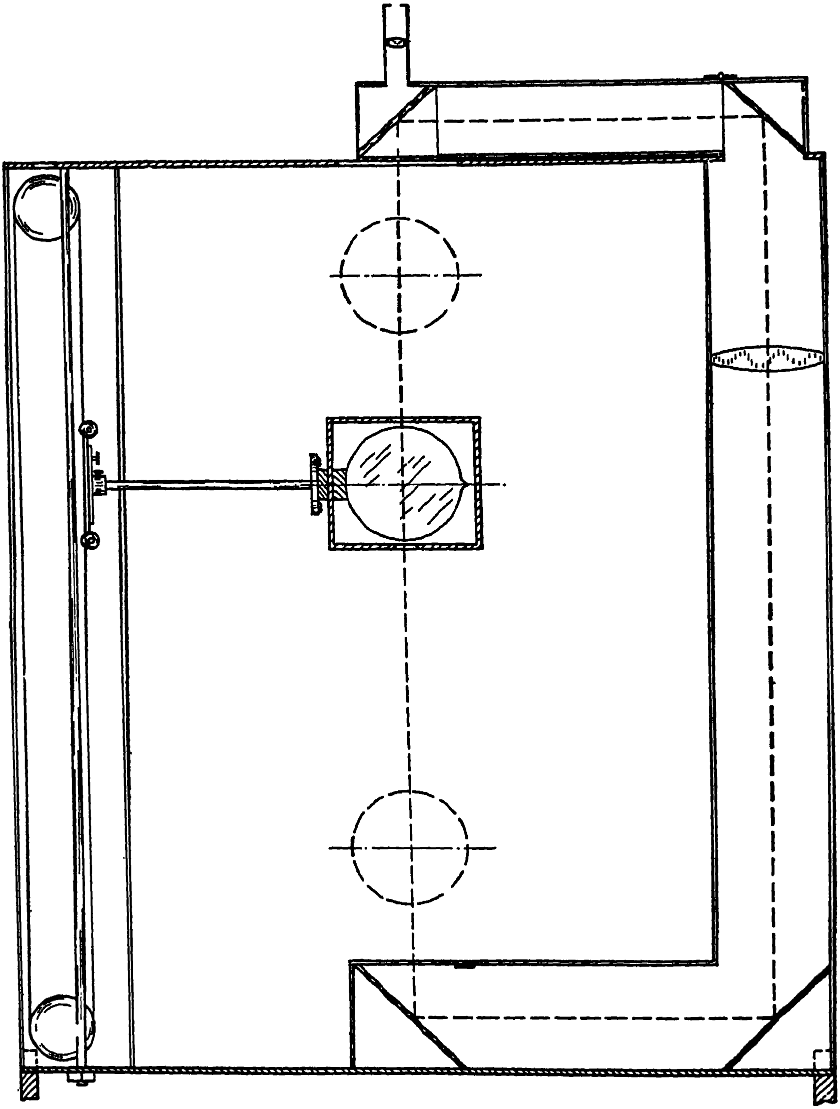

Fig. 184. The Capstaff-Green densitometer.

available, such as the Bunsen grease spot or the Lummer-Brodhun head. An intensity balance may be achieved by moving the head back and forth between the two sources or by moving the head and one source at the same time, the other source being fixed. A density is measured by making an intensity balance first with both sources unscreened and then with one source screened by the deposit to be measured. From the readings of distance made in the two cases and application of the inverse square law, the transmission of the deposit can be computed, and from that value the density. Such an instrument is clumsy to use, and the light sources require continual attention.

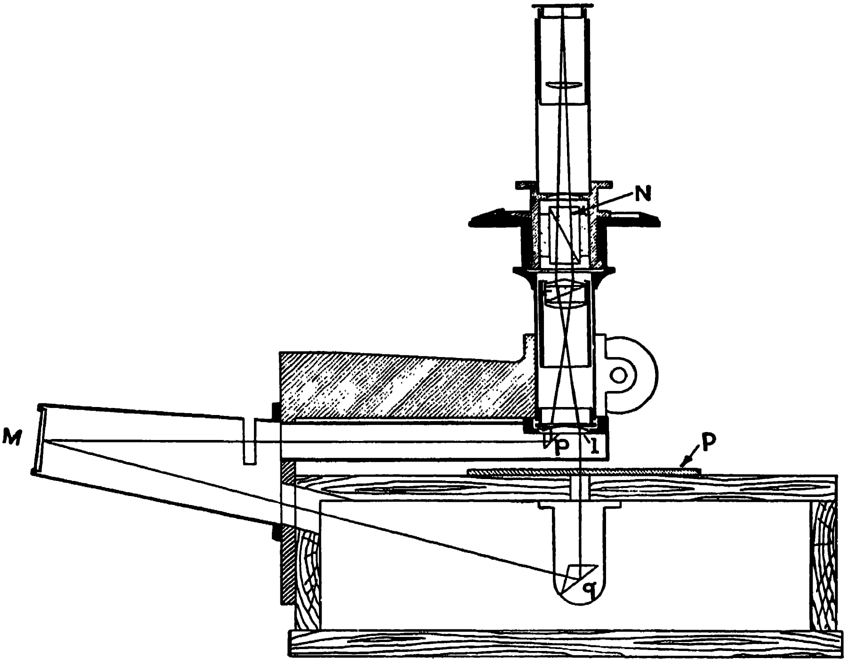

FIG. 185. Diagram of the Martens photometer.

A more convenient form of the bench photometer is that designed by Benson, Ferguson, and Renwick.[28] The light source and photometer head are fixed at one end, and equalization is obtained by means of sliding mirrors. A later bench instrument designed by Ferguson uses two lamps and is designed so that the intensity of the field is constant, whatever the density read. An instrument of this type for measuring very small areas of motion-picture film was designed by Capstaff and Green.[29] The optical arrangement of this instrument is shown in Figure 184.

Densitometers of the bench type have been displaced very largely by instruments depending upon polarization for the equalization of the two fields. Sheppard and Mees adopted the Hüfner spectrophotometer and used it throughout their investigations.[30] The best-known and most generally useful polarization instrument is the Martens photometer,[31] the internal construction of which in its original form is shown in Figure 185. Light from the source, *M*, goes directly to the small prism, *p*, which is opposite one opening of the photometer head and, by means of the prism, *q*, through the negative, which is placed in the position, *P*, and then through the other opening in the photometer head, *l*. Both of these beams are polarized by means of the Wollaston prism, which splits the light into two components, each of which is polarized in a plane perpendicular to that of the plane of polarization of the other. On the upper face of the Wollaston prism is cemented a Fresnel biprism, which forms the photometric field. The analyzing prism, *N*, is of the Nicol type. Equalization of the two beams is obtained by rotating the prism, *N*; the relation of the intensities transmitted through the two openings is given by the equation

$$\frac{I}{I'} = \frac{\mathrm{Tan}^2\, a'}{\mathrm{Tan}^2\, a},$$

where a and a' are the settings of the prism with and without the negative in position. The illumination system for the instrument has undergone modifications at the hands of various workers,[32] but for most photographic measurements it is convenient to use the head [33] without any prism system under the openings, illumination being obtained from a box covered with opal glass.

For reading very high photographic densities and, indeed, for general densitometry wherever there is sufficient work to justify such an instrument, one designed by Jones is of very great value.[34] The plan is shown in Figure 186. A powerful light source, *A*, sends two beams to the photometric cube, *K*; one, directly through the opal glass, *M*, on which is placed the negative to be measured, and the other to the opal glass *H*, through an arrangement of lenses and prisms in the path of which is interposed an adjustable sector diaphragm, *E*, placed between two lenses, *B*, so that the intensity of the beam transmitted can be adjusted by varying the angular opening of the sector. A rotating sector wheel of fixed aperture, *C*, can be placed in either beam to extend the range, which can be still further extended by diaphragm stops inserted in the collimated beam between the components of the lens, *F*. Diffuse densities as high as 8 can be read, only 1/100,000,000th of the incident light being transmitted, while for specular densities the scale can be extended to densities of 10. For the measurement of very high densities, this instrument is invaluable, and it is a most convenient densitometer for general laboratory work.

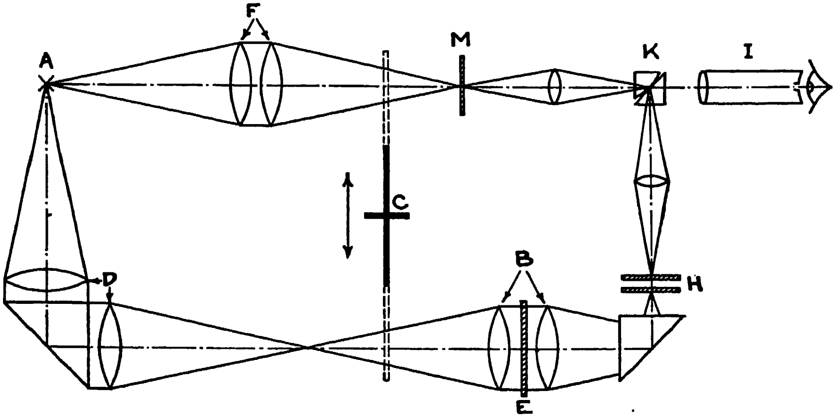

FIG. 186. Optical system of the Jones high-intensity densitometer.

Many of the densitometers used in photographic work are really comparators in which a photometric device is used to compare the density to be measured with a calibrated wedge or series of densities. One of the first of these instruments was recommended by Abney for astronomical work.[35] The Hartmann microdensitometer,[36] which is used extensively in astronomical photometry, is a wedge comparator used with microscopes, so that a very small field can be measured. Renwick,[37] in 1910, described a convenient form of density comparator using a neutral glass wedge. In 1911, Sanger-Shepherd[38] patented a simple form of wedge comparator, and Ferguson[39] also described one.

A valuable development in wedge comparators was the *densograph*, invented by Goldberg.[40] In this instrument, the characteristic curve is outlined on co-ordinate paper by a series of points, each corresponding to a setting of the comparison wedge to balance the density of the plate to be measured. The sensitometer exposure is generally made through the wedge to be used in measuring, and the densograph thus provides a very simple method of plotting the characteristic curve if great accuracy is not required.

Simple forms of density comparators are those of Ferguson [41] and Capstaff and Purdy,[42] the latter instrument being widely used. The arrangement of the essential parts is shown diagrammatically in Figure 187, and a photograph of the instrument in Figure 188. The light source, *A*, illuminates the small disk of opal glass, *H*, placed in contact with the photographic density. The light source, *A*, also furnishes the comparison beam, this comparison beam being reflected by the mirrors, *B* and *D*, into the photometric field-forming device composed of *F* and *G*. A photographic wedge for decreasing the intensity of the light illuminating the density by a known amount is placed between the lamp, *A*, and the density, *H*, as indicated at *W*. A suitable eyepiece, *J*, for viewing the photometric field is provided. The lamp, *A*, is mounted on the end of an arm, the position of which is controlled by the screw, *K*. By rotating this screw, the distance between the light source, *A*, and the opal glass, *H*, may

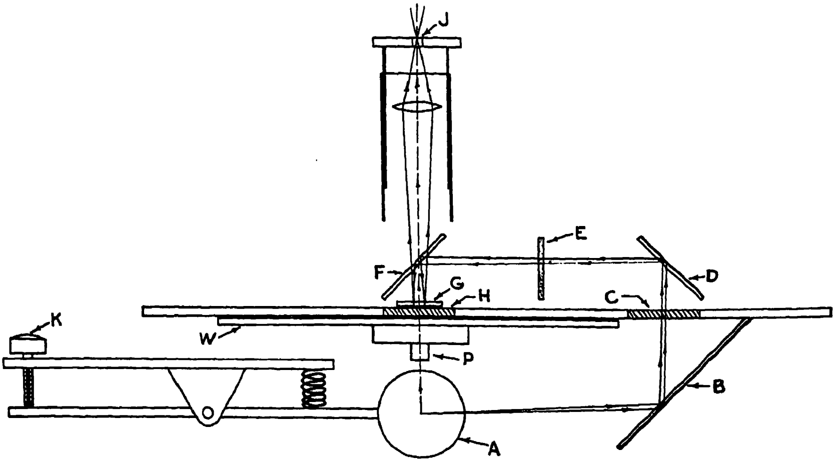

FIG. 187. Diagram of the Capstaff-Purdy densitometer.

be varied; and hence the illumination upon the density is controlled to some extent. Movement of the lamp in this manner does not appreciably change the distance between the lamp, *A*, and plate, *F*, and therefore does not change the illumination in the comparison part of the photometric field so that the adjustment may be used for setting the zero point of the instrument. The photographic wedge, *W*, for controlling the illumination incident on the opal glass, *H*, is circular and is mounted so that it may be rotated on the pin, *P*. It is made by copying a circular wedge cast in gray dyed gelatin onto a photographic plate. To facilitate turning, the edge of the wedge projects about ⅛ inch beyond the instrument cover. The beam of light, after passing through the wedge, falls upon the opal glass, *H*, and the density to be measured is laid on this diffusing screen. The photometric head consists of a glass plate, *F*, set at an angle of 45° to the comparison beam and so placed that the light from the mirror system is reflected to the base of the head. The two surfaces

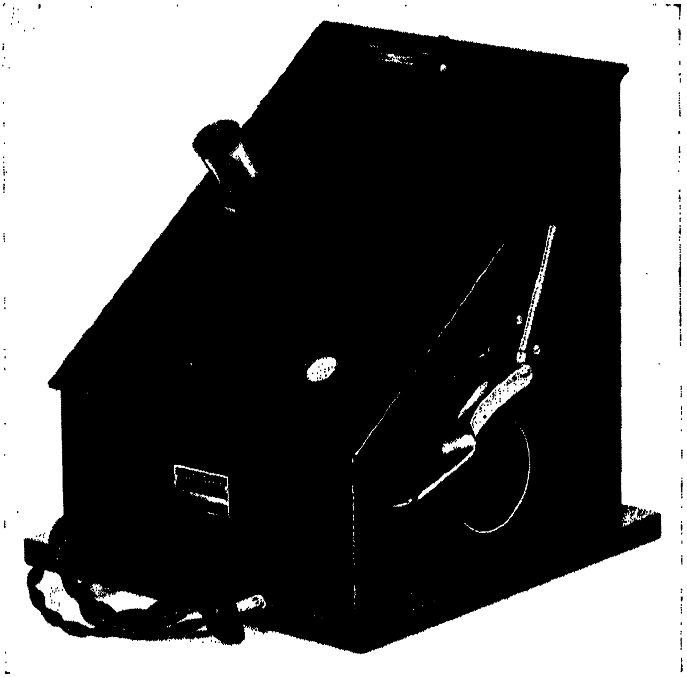

FIG. 188. The Capstaff-Purdy densitometer.

of this plate reflect sufficient light, about 10 per cent, to furnish the comparison beam. To insure the illumination on the comparison part of the photometric field being uniform, a piece of opal glass, *C*, is placed between the mirrors, *B* and *D*, and a piece of ground glass, *E*, is placed between mirrors, *D* and *F*. In the base of the photometric head is a piece of plane silver mirror, *G*, with its silver side toward the opal glass, *H*. The silver is removed from a circular area of ½ square millimeter in the center. The observer looking through the eyepiece, *J*, therefore, sees a circular spot illuminated by the opal glass, *H*, and surrounded by a comparison field illuminated from the mirrors, *B*, *D*, *F*, and *G*. The photographic wedge, *W*, must, of course, be precisely calibrated, and a suitable scale is attached to it to show the effective density of the wedge at any particular point. Through a small window, the density values on the calibrated wedge may be conveniently read during the use of the instrument. The eyepiece, the photometric head, and the mirror, *D*, are mounted in an L-shaped element which is hinged so that it may be lifted out of the way to facilitate placing the photographic density in position over the opal glass, *H*.

Photoelectric Densitometers

Many attempts have been made to substitute radiation-sensitive devices for the human eye in the measurement of density. The advantages are: the elimination of visual fatigue, the attainment of higher precision, and the increase of reading speed. The accuracy of visual reading cannot exceed 0.008 in density because of the inherent characteristics of the eye. Even experts can make only five or six readings a minute and that for only a limited period.

The earliest physical densitometers were designed by astronomers and spectroscopists who were interested in measuring stellar images or spectrum plates. Stetson[43] described an instrument incorporating a thermopile and galvanometer, the galvanometer deflection being read with and without the material in place to determine transmission. Moll[44] with a new, quickly acting thermopile and short-period galvanometer devised an excellent photographic recording instrument which is widely used for the measurement of spectrograms. Harrison, Pettit and Nicholson, and many others developed and refined thermoelectric densitometry. Harrison [45] discussed the various types of physical densitometers and described a single thermocouple instrument with which he achieved an accuracy of one half of one per cent—about 0.002 in density.

Thermoelectric instruments have little advantage in speed over visual photometers. They are affected by temperature variation, are of low sensitivity, and most of their response is in the extremely long wave length region of the spectrum and is therefore of little value in measuring spectrally selective materials. Other thermal radiation measuring devices—bolometers, radiomicrometers, and radiometers—suffer from the same defects, though all of them have been used in densitometers.

Photoelectric cells are free from most of the shortcomings of the thermal devices; but most of them, especially the earlier types, are less stable than thermopiles. This instability was a disadvantage in the simple deflection-reading arrangements employed by the makers of thermoelectric densitometers. Most of the photoelectric instruments make use of a method employing the cell to ascertain the equality of two light intensities. One beam is modulated in a known manner; and the setting of the modulating device, frequently an absorbing optical wedge, is read at the position of balance for the two beams.

One of the earlier examples of a balanced-beam photoelectric densitometer is described by Dobson.[46] A diagram of his instrument is shown in Figure 189. Light from the source, *E*, is picked up alternately by two optical systems, one of which focuses the filament on the sample, *T*, to be measured, while the second beam passes through an adjustable wedge, *W*. The shutter, *R*, rotates around the lamp four or five times a second, and the cell, *P*, is illuminated by one or the other. The cell output passes into a fiber electrometer, which vibrates visibly if the state of unbalance between the beams exceeds 0.1 per cent, a state which corresponds to about 0.0004 in density. There is little doubt that Dobson's instrument represented a real gain in stability over the original photoelectric registering photometer of Koch,[47] which was a direct deflection instrument; but its delicacy was a drawback.

Toy and Rawling[48] tried to improve Dobson's instrument by substituting a photoresistive selenium cell for the photoemissive cell. Their optical system and method of light modulation were similar to Dobson's. The current available with the selenium cell is much greater than from the photoemissive type, and consequently a less sensitive indicating instrument can be used. Unfortunately, it has other weaknesses, such as great instability and considerably more lag than the photoemissive type.

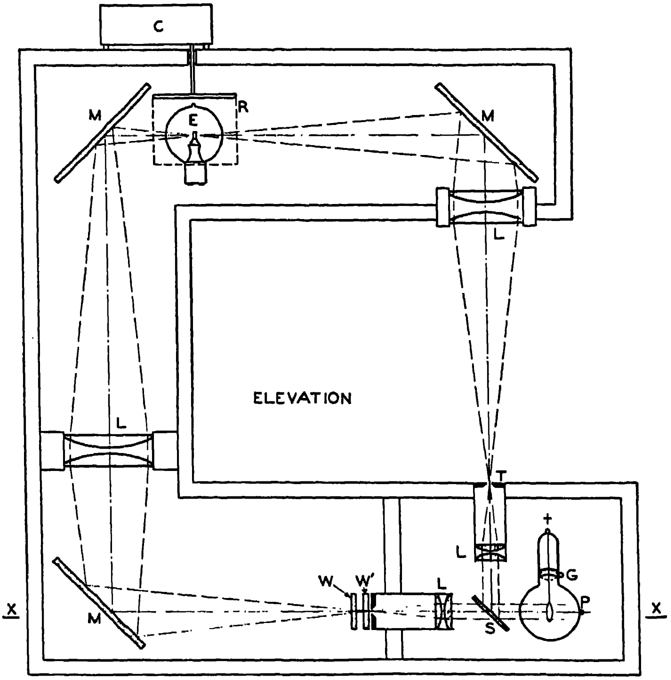

FIG. 189. Diagram of the Dobson photoelectric densitometer.

Another photoresistive type of cell, using thalofide instead of selenium, was used by Schoen[49] for the measurement of low densities; but no photoresistive cell instrument has been an unqualified success, and in most of the more recent designs the photoemissive cell has been used because of improvements in photoemissive cells and in the ruggedness and stability of amplifier circuits. A complete list of these instruments would be very long, and a brief mention of the characteristics of a few will suffice.

The British Photographic Research densitometer[50] has two symmetrical optical beams. Measurements are made by a neutral wedge having a density range up to 4.0. It has a capacity of 1000 readings a day.

Lindsay and Wolfe[51] describe an instrument in which the amount of amplification required for a predetermined deflection on a galvanometer gives the reading. The light to the photocell is interrupted by a rotating sector plate, so that an alternating-current logarithmic amplifier may be used. This has been developed by Frayne and Crane[52] into a densitometer in which an integrating sphere collects the light transmitted by the density. The measuring photocell is located within the sphere.

White[53] uses an ingenious arrangement in which the density to be measured is illuminated through a circular optical wedge which is continuously rotated; the amplified photocurrent varies with the transmitted intensity. The amplifier circuit flashes a stroboscopic light source which illuminates the density scale on the wedge at the point where the reading should be made.

The barrier layer, self-generating, photoelectric cell introduced a new factor into physical densitometry. This cell combines many of the good features of other radiation measuring devices with few of their limitations. It has stability and simplicity comparable with the thermopile, current output comparable with the photoresistive cells, reading speed comparable with photoemissive cells, and spectral response lying almost entirely in the visible spectrum. It is admirably fitted to substitute for the thermopile in the direct-reading deflection type of instrument. Numerous densitometers consisting merely of a light source, a barrier layer cell, and a microammeter have been described. Since the response of the cell is approximately a linear function of the illumination, these simple densitometers have the same limitation as direct-reading thermopile instruments in that the accuracy decreases rapidly as the density increases. Single-scale direct-reading instruments are not of much value for the measurement of densities over 1.3.

The Weston Electrical Instrument Company has partially overcome this scale condensation by producing a barrier layer cell densitometer with a galvanometer having an expanded scale at the low deflection end.[54] This instrument is calibrated to a density of 3.0 and can be read with considerable accuracy up to 2.0.

Tuttle[55] investigated the photometric possibilities of using two barrier layer cells with potentials opposed in a null circuit. He found that if each member of a pair of matched cells was illuminated by an intensity such that the sum of their opposed potentials across a galvanometer was zero, the combination would be stable for an indefinite period. The limitation of the stability seems to be that of the galvanometer itself. Tuttle concluded that such a balanced circuit is capable of detecting with certainty an intensity variation of less than 0.1 per cent. This is true over a wide range in the intensity level and the color temperature of the source. This system of photometric balancing seems to be one of the most accurate and dependable and is completely independent of variations in the lamp voltage. Tuttle used the scheme to produce a recording physical densitometer of high speed and accuracy having a range from 0.0 to 3.0. The optical system is illustrated in Figure 190. Two beams from a single source reach the two cells after passing through a right-angle prism. The totally reflected beam passes through a variable optical diaphragm and the density to be measured before it reaches the measuring cell. The second

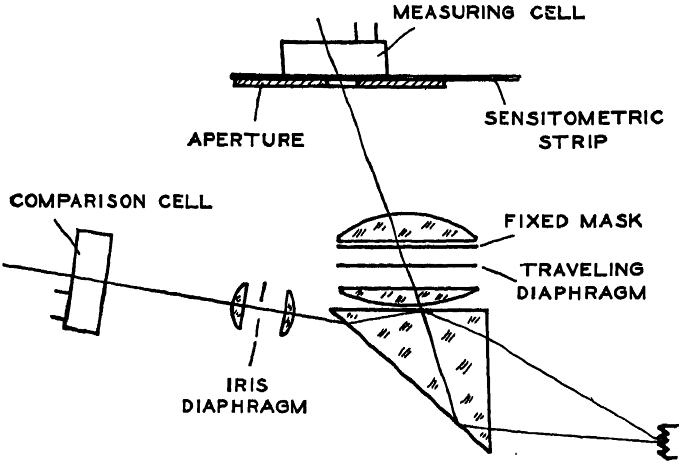

Fig. 190. Optical system of a recording physical densitometer using Barrier cells. (Tuttle.)

beam, reflected from the top surface of the prism, reaches the comparison cell. The light-modulating device is the variable aperture shown in Figure 191. This replaces the usual absorbing optical wedge and has the advantage that it is absolutely permanent and spectrally non-selective. The instrument reads and plots data from Eastman II–B sensitometer strips (page 614). An electric spark passes through the paper to record the data, the indexing of the graph paper and strip being entirely automatic (Figure 192). Tuttle and Russell[56] studied the performance of the instrument in comparison with visual reading and found the average error of the physical instrument less than half that of the visual method. The latest instruments of this type have a capacity of about 25,000 readings a day.

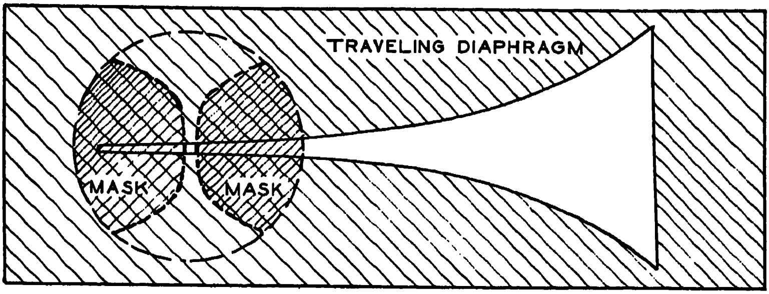

Fig. 191. Diagram of light-modulating device for recording physical densitometer.

In some physical densitometers, little regard is paid to factors mentioned in the early part of this chapter. There it was pointed out that the numerical value of a density is dependent upon several of the characteristics of the optical system by which it is measured. In physical densitometers, the radiation measuring device is an important part of the optical system and one which is frequently different from the visual measuring device which it replaces.

Selwyn and Pitt[13] are responsible for a thorough discussion of this subject, as a result of which they recommend that:

1. To avoid discrepancies arising from interreflections between optical parts and the sample, the base density should be reckoned as zero.

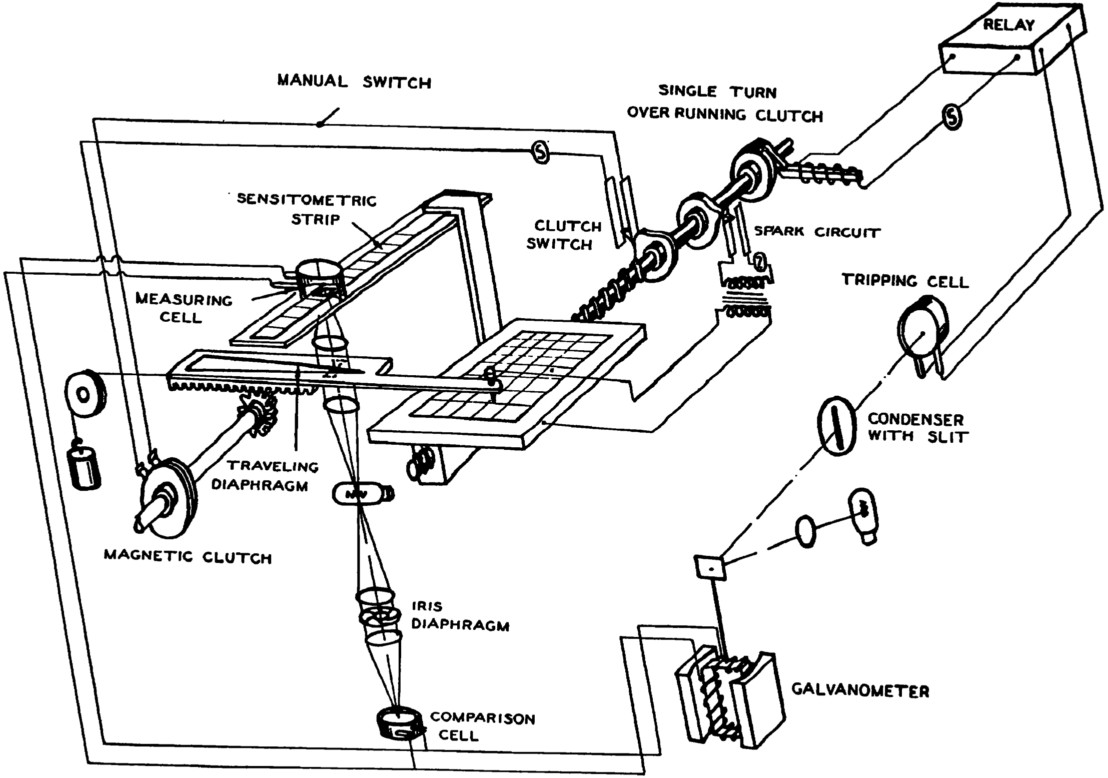

FIG. 192. Diagram of recording physical densitometer.

2. Opal glass should be placed between the photocell and the material being measured to keep the distribution on the cell constant.
3. The angle of the cone of light collected by the photocell should be kept small to avoid residual errors from the variation of distribution.

Hiatt and Tuttle[57] discuss the special case of a barrier layer cell as the receiving element. They found that, with the flat surface of the cell close to the sample, a close approximation to diffuse density is achieved with no diffusion in the system.

Tuttle and McFarlane[58] dealt with the special case of density measurement in sound-reproducer systems, showing the dependence of density upon the cone angle of collection.

THE MEASUREMENT OF DENSITY BY REFLECTION

If a photographic image is produced upon an opaque support, as in the case of prints upon paper, it is necessary to measure the optical properties of the image by the light reflected from it. The relation between the light transmission of a photographic image and the light reflected from it upon an opaque support was studied by Renwick,[59] who expressed his measurements in terms of the logarithm of the ratio of the light reflected by the paper base to the light reflected by the image. Thus, the *reflection density* is assigned the value $D_R = \log \frac{1}{R}$, analogous to the expression for the density of transparent materials, $D = \log \frac{1}{T}$. According to Jones, Nutting, and Mees,[60] the relation between the reflection and the transmission is given by the equation

$$D = \log \frac{1}{(1 - C)T^2 + C},$$

C being a constant. This equation was criticized by Renwick,[61] who applied to the problem a study of the behavior of scattering media by Channon, Renwick, and Storr.[62] In applying his results to practical measurements, however, Renwick used approximations which led to the use of an expression differing from that used by Jones, Nutting, and Mees only in the meaning of the constants. The matter has been investigated further by F. and A. Urbach,[63] who find that a slightly modified expression represents their experimental results within the limits of error.

The character of the optical system of a reflection densitometer has just as important an effect upon the numerical value of a density as it does in transmission densitometry. McFarlane[64] lists eight optical factors which influence the measured value of reflection density, but the chief of these concerns the distribution of the reflected light. Light reflected from a photographic print has two components, one specular and the other diffuse. The value of the reflection coefficient depends upon the relative amounts of these two components accepted by the measuring element of the densitometer. For the best results when a photographic print is viewed, it is necessary for the conditions of lighting and the angle of view to be such that the smallest possible amount of the specularly reflected light enters the observer's eye. If these conditions are not fulfilled, a more or less distinct image of the source of illumination will be seen on the picture, thus producing glare and preventing a satisfactory viewing of the picture. To conform to this practical print-viewing situation, the conditions of photographic paper densitometry have been set up to throw out the principal specular component and to measure diffusely reflected light.

Owen and Sanders[65] show that, because of the regular arrangement of fibers in machine-coated photographic paper, it is impossible to avoid all of the specularly reflected light unless the paper sample is oriented correctly with respect to the incident beam; *i.e.*, with the fibers in the plane of the beam. The magnitude of the effect is not very great, and it was disregarded in paper densitometry up to the time of the Owen and Sanders' article.

Various forms of bench and wedge photometers* may be adapted to the measurement of the light reflected from papers. Jones, Nutting, and Mees[60] used a modified Bechstein illuminometer, of which a diagram is shown in Figure 193. The source of light, *E*, is a concentrated filament, 100-watt tungsten lamp. The light from this illuminates the screen, *C*, of thin, solid opal

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* Photometers using polarized light must be used with proper precautions to make certain that light reflected from the paper surface is not polarized to an extent which will vitiate the results.

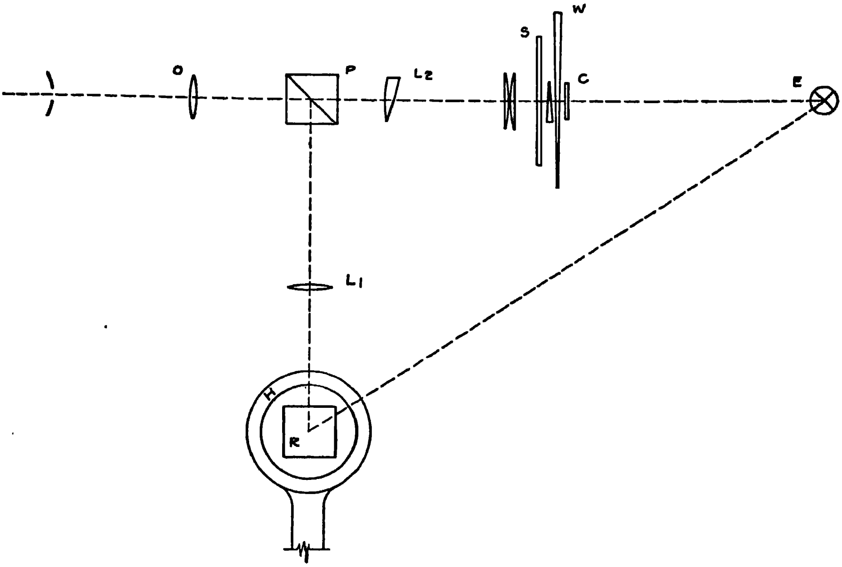

FIG. 193. Optical system of modified Bechstein illuminometer.

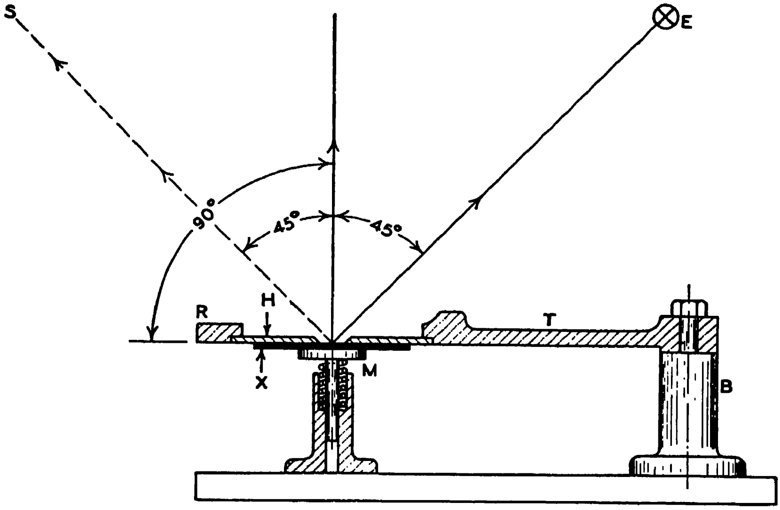

FIG. 194. Diagram of paper holder for reflectometer.

glass. This screen is viewed through the objective, *O*, the photometer cube, *P*, the rotating lens, L_2, and the stationary adjustable sector, *S*. The lens, L_2, is rotated so that the opening of the sector, *S*, is integrated over the field, and the intensity of the beam transmitted by L_2 is therefore proportional to the aperture of the sector. This forms the outer field of the photometer cube, *P*. The inner field consists of an image of the photographic print to be measured, which is placed in a suitable holder, *H*, on the table directly under the right-angle prism, *R*, an image of the small portion to be measured being formed on the cube by the lens, L_1. The surface of which the reflecting power is being measured is illuminated by the *same* source, *E*, which is used as a comparison source; therefore, variations in the intensity of this source are of no importance. The holder, of which a cross section is shown in Figure 194, consists of a metal ring, *H*, carried at the end of an arm, *T*, projecting from the pillar, *B*. In the ring is fitted a thin metal plate, in the center of which is an opening 4 millimeters square with edges beveled and carefully blackened to prevent reflection. The sample, *X*, to be measured is placed under this opening and pressed against the plate, *T*, by a flat-topped, spring-actuated plunger, *M*. In this way, the paper is held perfectly flat and in a horizontal plane. The horizontal plane through *EPR* (Figure 193) occupies a position in space about 25 centimeters above the plane of the paper in the holder, and the distance from *P* to *E* is such that the light from *E* is incident on the sample in the holder at an angle of 45°. Since the right-angle prism, *R*, through which the light enters the photometer cube is directly above the sample in the holder and the paper is held in a horizontal plane, it is evident that the brightness of the image in the photometer cube is due to light that leaves the paper normal to the surface. Figure 194 shows the conditions diagrammatically. Light from the source, *E*, is incident on the paper at 45°. The major part of the specular reflection goes in the direction *S* and is thus thrown out of consideration; while the light that illuminates the photometric field is reflected normally to the surface of the print. Thus, the conditions of illumination and direction of observation used in measuring the reflecting power are very similar to those existing when a picture is viewed by an observer.

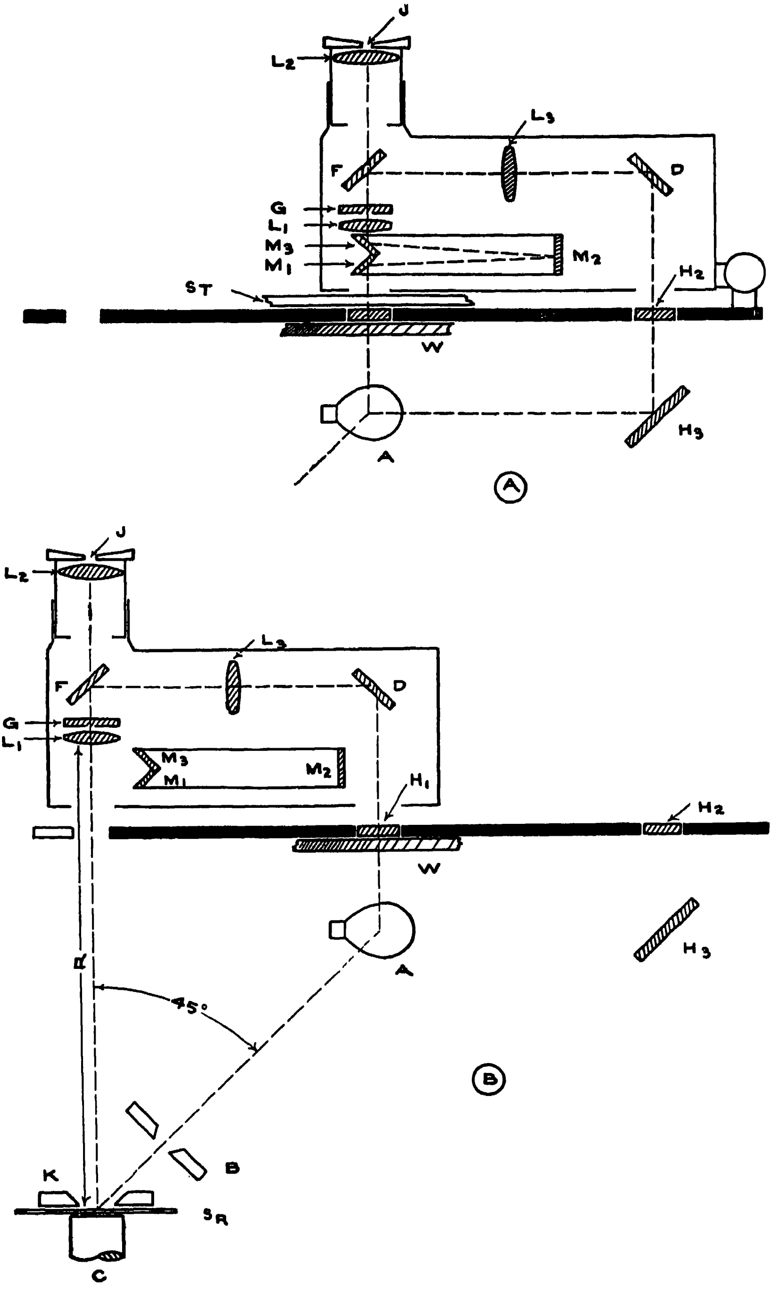

FIG. 195. Optical system of combination transmission-reflection densitometer.

In this instrument a portion of the paper that has been developed and fixed without exposure is placed under the opening in the holder, *H*. The wedge, *W*, is set so that the two halves of the field balance, and the wedge is clamped in position. When other portions of the print are placed under the opening, the sector is set again so as to give a balance in the field, and the value of the reflecting power (in percentage) is read directly from the scale attached to the sector.

McFarlane[64] adapted the Capstaff-Purdy transmission densitometer to the measurement of reflection densities, and his optical system was later incorporated by Morrison and McFarlane[66] in a combination transmission-reflection densitometer, from which the diagrammatic sketch of the two optical systems is taken (Figure 195). The lower half (*B*) shows the manner in which the instrument is used for reflection measurements. The light source, *A*, illuminates the paper sample at an angle of 45°. The normally reflected light is collected by the lens, L_1, which illuminates the clear, central aperture of the mirror, *G*. The comparison beam passes through the circular photographic wedge, *W*, and is reflected by the mirror, *D*, and glass plate, *F*, to the outer reflecting portion of the mirror, *G*, which forms the photometric field.

Physical densitometers have been applied to reflection as well as to transmission density measurements. Owen and Davies,[67] after a careful study of the possible sources of discrepancy between visual and photoelectric reflection density readings, set up an instrument using a neutral wedge. They were able to avoid error due to visual and photoelectric color sensitivity differences by using a suitable filter. They were also able to increase the collection angle to a point where sufficient sensitivity was obtained without serious departure from visual values obtained with a smaller collection angle.

The essential parts of the optical system of a new photoelectric densitometer designed by Tuttle are shown in Figure 196. A concentrated filament source, *S*, is imaged by the lens, L_1, on an area of a print at *P*. Before reaching *P*, the light beam is reflected once at plane mirror M_1 and again at mirror M_2, so that it is incident on *P* at an angle of 45°. The two mirrors are mounted in the interior of a drum driven from its periphery so that it revolves about the optical axis of the instrument. The incident beam is rotated several times a second so that light reaches the sample from every direction but always at an angle of 45° to the normal. The normally reflected light enters a right-angle prism, N, and is concentrated by a lens, L_2, onto a barrier layer cell, C_1. The output of the cell, C_1, as measured by a galvanometer whose period is several times that of the rotating beam, is an average value for all angles of incidence. Thus, the effect of paper texture, which was pointed out by Owen and Sanders, is taken care of. A second beam from the source, S, is imaged by the lens, L_3, onto a piece of unexposed paper, also at an angle of 45°. This sample is rotated by the motor, E. The cell, C_2, integrates the light coming normally from the sample. C_2 is opposed in polarity by C_1. Light on C_1 is modulated by the diaphragm in L_1. This diaphragm is similar to that in the automatic transmission densitometer (Figure 191), and the whole photoelectric and automatic control system of the reflection recording densitometer is very similar to the instrument described on page 664.

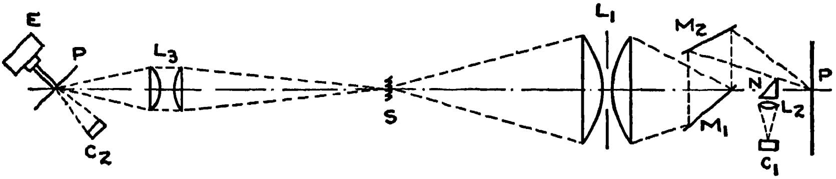

FIG. 196. Optical system of automatic paper densitometer.

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CHAPTER XVIII

THE MEASUREMENT OF SPECTRAL SENSITIVITY

A knowledge of the way in which the sensitivity of a photographic material is distributed throughout the spectrum, in the ultraviolet and infrared as well as the visual regions, is of importance from many points of view. The correct rendering of colored objects on the black-to-white tone scale is conditioned by the spectral sensitivity of the material. As early as 1882, Abney[1] studied the spectral sensitivity of photographic materials by exposing them in a spectroscope. By plotting densities determined by visual estimation against wave length, he obtained a curve of spectral sensitivity. He later improved the method, and in 1888[2] he suggested impressing on the same plate an exposure to a spectrum and a series of known exposures to white light. The opacities of the spectrum exposures were then measured and interpolated between those of the white-light exposures. He thus obtained a curve showing the equivalent spectral intensities for various wave lengths. Since that time, many methods have been proposed for the measurement and expression of color sensitivity.

All methods used for obtaining information as to the spectral sensitivity of photographic materials involve the isolation of more or less narrow spectral bands and the observation, either qualitatively or quantitatively, of the response produced when the material is exposed to these more or less homogeneous radiations. For this purpose, a wide variety of special instruments—monochromatic sensitometers, spectrographs, tricolor tablets, ratiometers, color charts, and filter assemblies—have been devised. The more refined methods involve the dispersion of radiation by suitable elements, such as prisms or diffraction gratings. Instruments of this type may be divided into two general classes. The first includes those in which the photographic material is exposed to the entire spectrum at the same time; in the second, a single, narrow band of practically homogeneous radiation is isolated, to which the photographic material is exposed as in the sensitometers already described. While it is impossible to draw a strict line of demarcation, the term *monochromatic sensitometer* is usually applied to instruments of the second class, while the term *spectrograph* is used in reference to those of the first class.

MONOCHROMATIC SENSITOMETERS

An optical system for isolating monochromatic radiation of high spectral purity is used in the monochromatic sensitometer described by Jones and Sandvik.[3] This consists essentially of two quartz monochromatic illuminators. The radiation emerging from the exit slit of the first monochromatic illuminator passes into the second (Figure 197). In this way, practically all of the stray radiation is eliminated, so that the radiation emerging from the exit slit of the second monochromatic illumi-

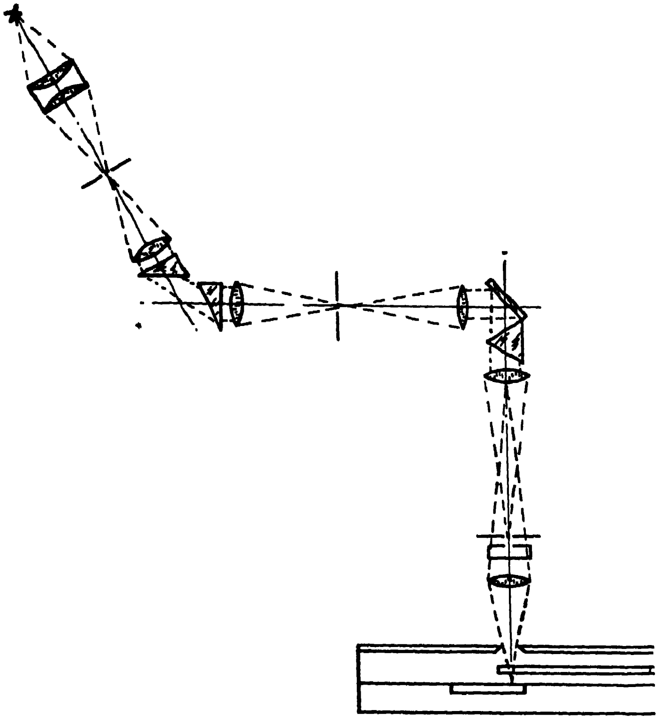

FIG. 197. Optical system of monochromatic sensitometer.

nator is entirely of the wave length indicated by the wave length drums of the two instruments. High purity is the prime requisite for work of this kind, especially for those spectral regions where the energy from the light source or the sensitivity of the material is low compared with that in other spectral regions. After being isolated, the homogeneous radiation is allowed to fall on the photographic plate and, by means of a suitable mechanism, the time of exposure is varied in a known manner. The method adopted by Jones and Sandvik employs a sector disk of special type (Figure 198) in which the apertures are arranged spirally around the axis of rotation, and the entire disk is moved laterally while rotating at a uniform angular velocity. By utilizing the spiral arrangement of apertures, the maximum exposure time corresponds to an angular rotation of 720° of the shutter disk. In this way, twelve exposures increasing by consecutive powers of two are given, the range of times being from 1 to 2048; and an exposed sensitometric strip of the conventional

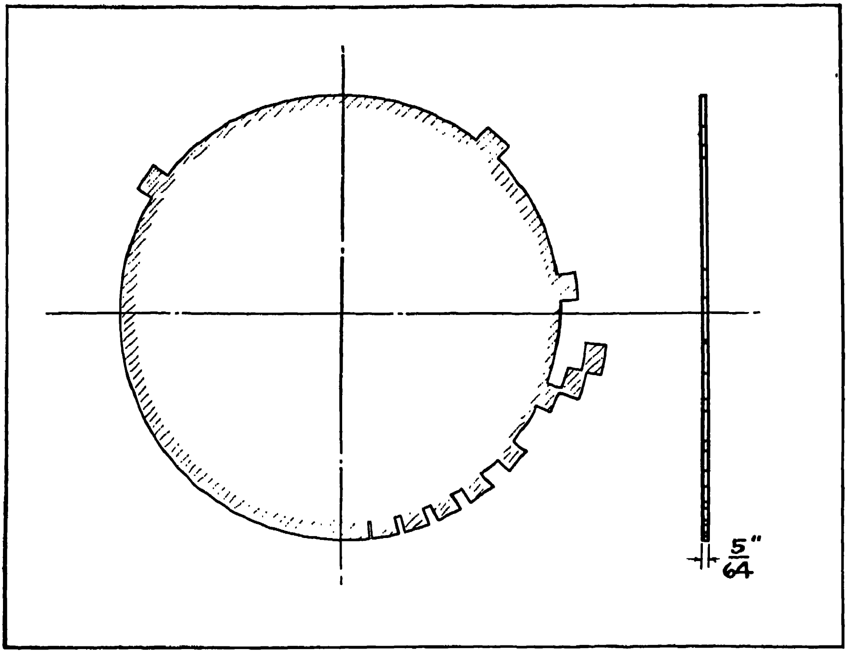

Fig. 198. Sector disk of monochromatic sensitometer.

type is obtained. After each step is exposed, the plate holder is moved automatically into place for the exposure of the next step.

The monochromatic sensitometer described above was made with quartz optics and especially adapted for use in the ultraviolet region of the spectrum. For the longer wave lengths, this instrument is less satisfactory because of the low dispersion of quartz toward the red end of the spectrum; and a somewhat different instrument is desirable for the visible and near infrared spectrum. Such an instrument was described by Evans.[4] In this, the dispersing elements consist of replica gratings so arranged that a constant dispersion is obtained whatever the wave length. The exposing system in this instrument is arranged to give an intensity scale by using intermittent exposure. Two sector wheels are located just in front of the exposure plane. One has a single opening of 180° and performs a single revolution in 30 seconds, thus giving an exposure of 15 seconds' duration at all points of the exposure field. If longer exposures are required, the sector wheel can be stopped after it has performed half a revolution and then allowed to complete its revolution after the required time has elapsed. The other sector wheel, shown in Figure 199, contains a large number of radial apertures, their length graduated in nine steps, but all starting from the periphery. In this way, the sector wheel has nine concentric zones of apertures, the outer one transmitting half of the light, the next one quarter, and so on. The ninth zone admits 1/512 part only and is represented by a single slot. The sector wheel is driven by a motor at approximately fifty revolutions a second. As shown by Webb[5] (Chapter VI, p. 253), if a photographic material is given an intermittent exposure, the photographic effect will be the same as that of a continuous exposure of the same duration and intensity equal to the average intensity of the intermittent exposure, provided that the frequency of flash is above a certain critical frequency for such intensities, and the exposure scale used is thus exactly equivalent to an intensity scale.

By the use of a thermopile at the exit slit of the monochromator, the energy flux density of the monochromatic radiation may be measured. A thermopile-galvanometer combination of high sensitivity is required, and care must be exercised in making the energy measurements to obtain reliable and precise results. The determination of these energy values with the required precision is, perhaps, the most difficult step in the process of obtaining absolute values of spectral sensitivity.

The monochromatic sensitometer gives exposed strips of the conventional type. They are subjected to a series of increasing development times; and a complete family of characteristic curves is obtained for each wave length, the exposure values being expressed in terms of energy (ergs per unit area). From these may then be plotted curves showing the variation of sensitivity and γ with wave length throughout the spectrum.

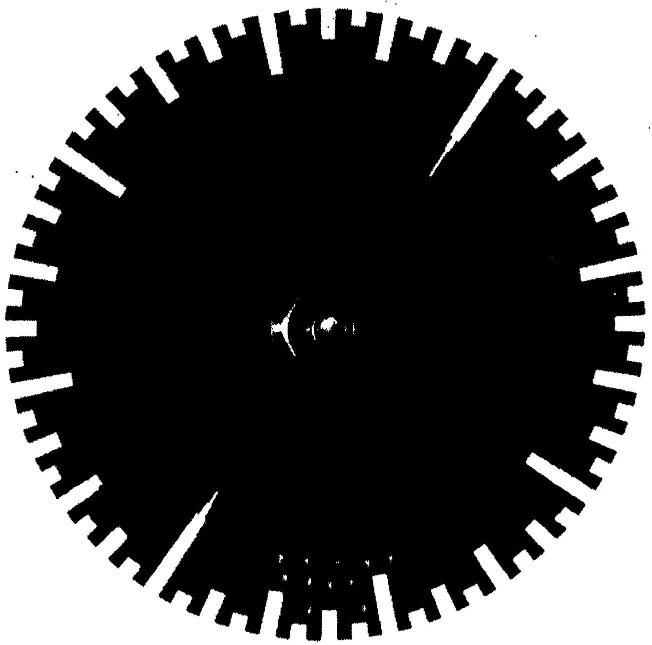

FIG. 199. Sector disk of radial type.

The variation of γ with wave length has been the subject of a number of investigations. The fact that photographic contrast changes with wave length was discovered independently by Abney[6] and Precht.[7] The matter was investigated in detail by Chapman Jones[8] on a number of different photographic plates; and he concluded that, in general, the contrast increases continuously from the ultraviolet to the red, the shape of the characteristic curve varying, with a shortening of the straight-line portion as wave length is increased. Abney did not confirm this result using pure silver salts instead of commercial emulsions. He found that the least steep gradation is that given by the monochromatic light to which the silver salt is most sensitive and that the gradation becomes steeper as the wave length employed departs in either direction from this point, the steepest gradation being given by the extreme red. Leimbach [9] found no change of gradation with wave length. A considerable number of publications on the subject are summarized by Ross,[10] particularly in relation to their application in astronomy. His conclusions are endorsed by all modern workers on the subject.

The relation of γ to wave length follows no general rule. It depends upon the emulsion and is complicated by the failure of the reciprocity law. Emulsions behave differently according to the way in which the different sizes of grains are sensitized by the dyes employed. Thus, if a dye sensitizes smaller grains selectively, it will change the gradation for the region for which it sensitizes compared with the spectral regions in which the sensitivity does not depend upon the presence of the dye. Some dyes produce notable changes in γ; others, very small changes in γ; so that it is impossible to make any general statement about the relation of γ to wave length for optically sensitized emulsions.

In Figure 200 the curves show the variation of γ with wave length for four different sensitizings of the same high-speed emulsion. *A* is the unsensitized emulsion, *B* the same emulsion sensitized to the green, and *C* and *D* are two panchromatic sensitizings. In Figure 201 the curves show the variation of γ with wave length for different sensitizings of a medium-speed emulsion, single dyes being used for sensitizing in this case. *A* is the unsensitized emulsion, *B* is sensitized with a pseudocyanine, sensitizing to the green, *C* with a merocyanine, *D* with a thiacarbocyanine sensitizing to the green and orange, and *E* with a dibenzthiacarbocyanine sensitizing to the red.*

The shape of the wave length sensitivity curve depends greatly upon the manner in which sensitivity is defined. For ordinary sensitometric purposes, sensitivity is expressed in terms of visual meter candle seconds. For the expression of monochromatic sensitometric results, it is obvious that this method is useless, and it is necessary to express exposure in terms of energy units.

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* For information regarding these dyes, see Chapters XXIII and XXIV.

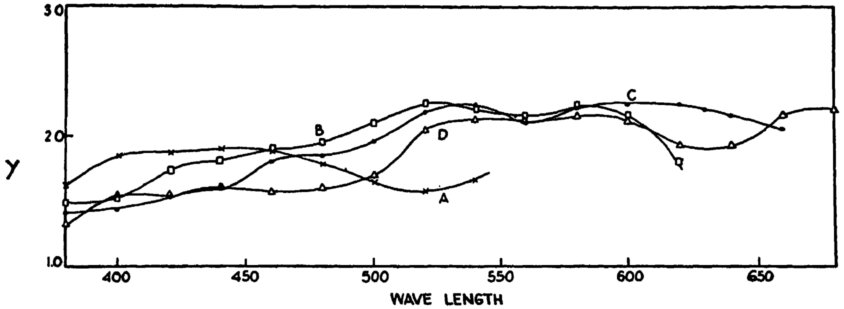

FIG. 200. Variation of γ with wave length for four sensitizings of a high-speed emulsion: *A*, unsensitized emulsion; *B*, sensitized to green light; *C* and *D*, panchromatic sensitizings.

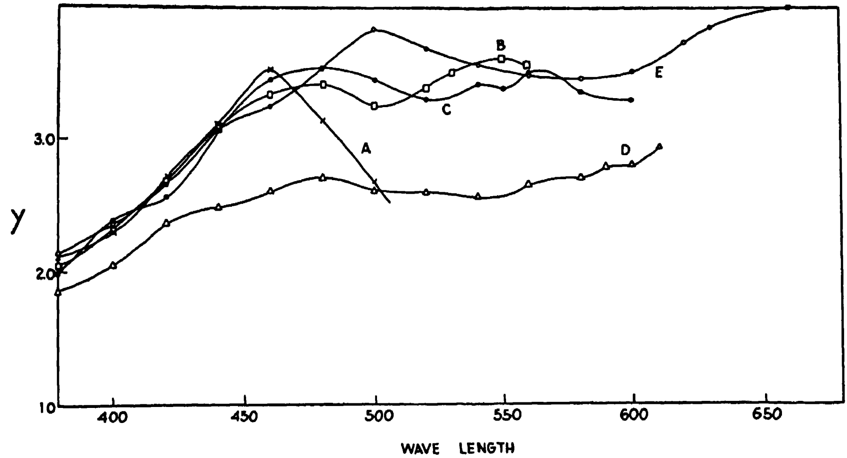

FIG. 201. Variation of γ with wave length for a medium-speed emulsion: *A*, unsensitized; *B*, sensitized with a pseudocyanine; *C*, sensitized with a merocyanine; *D*, sensitized with a thiacarbocyanine; *E*, sensitized with a dibenzthiacarbocyanine.

Exposure, therefore, may be expressed in terms of ergs (or other suitable energy units) per unit area.

A suitable method of expressing spectral sensitivity remains to be considered. It is possible, of course, to compute the sensitivity at various wave lengths in terms of reciprocal inertia.

By plotting reciprocal inertia values as a function of wave length, a spectral sensitivity curve is obtained; and for many purposes this method seems to be satisfactory. It should be pointed out, however, that spectral sensitivity can be expressed in other ways, and it is possible that some of these may be more useful from the practical point of view. If spectral sensitivity is defined in terms of the energy required to produce a density of unity for a fixed time of development, the shape of the spectral sensitivity curve is quite different from that based upon inertia. Moreover, if a higher density value is chosen, a still further modification occurs in the shape of the spectral sensitivity curve.

There does not seem to be any means of determining the most desirable mode of expressing spectral sensitivity; the particular problem in hand must probably be the deciding factor. For theoretical purposes, there is an advantage in defining spectral sensitivity in terms of the energy required to give a density of unity when development for all wave lengths is carried to a γ of unity. For practical purposes, however, a fixed development time seems preferable. In order to discount somewhat the misleading effects due to the variation of γ, the determination of the energy per unit area required to give a density of unity in a fixed time of development seems most satisfactory as a mode of expressing spectral sensitivity. The most suitable development time is probably that which, for a sensitometric strip exposed to white light, produces a γ approximately equal to that to which the material is usually developed in practice.

In Figure 202 are shown the spectral sensitivity curves of a panchromatic film expressed by various methods. In curve *A* the inverse of the inertia values (measured in ergs per square centimeter) is plotted against the wave length. In curve *B*, the sensitivity is expressed as the reciprocal of the exposure (measured in ergs per square centimeter) required to produce a constant density for uniform development, the degree of development being that required to give a γ of unity for white-light exposures. In curve *C*, the same method of expression is employed as for curve *B*, but the logarithm of the sensitivity is plotted. In curve *D*, the sensitivity is expressed as in curve *C*, but the development at every point of the curve is that required to produce a γ of unity.

It should be borne in mind that the spectral sensitivity curve plotted in accordance with the specifications given in the last paragraph represents the characteristics of the photographic material itself, quite apart from any consideration of the energy distribution in the light source used. The curve thus obtained shows the response of the material when used with a light source emitting the same amount of energy at all wave lengths. In practice, light sources used for photography depart greatly from this condition of an "equal energy" spectrum. Figures 203 and 204 illustrate the strong influence which the spectral composition of the radiation can exert on color rendition. In Figure 203 is shown the sensitivity curve of a panchromatic film plotted on an equal energy basis. In Figure 204 the dotted curve, *A*, represents the distribution of energy in the radiation emitted by an incandescent tungsten filament operating at a color temperature of 3000°, which is an efficiency frequently met in practice. The curve *B* is obtained by multiplying, wave length by wave length, the ordinates of curve *A* by the ordinates of the spectral sensitivity curve of the material and represents the sensitivity curve of the film to the tungsten light source.

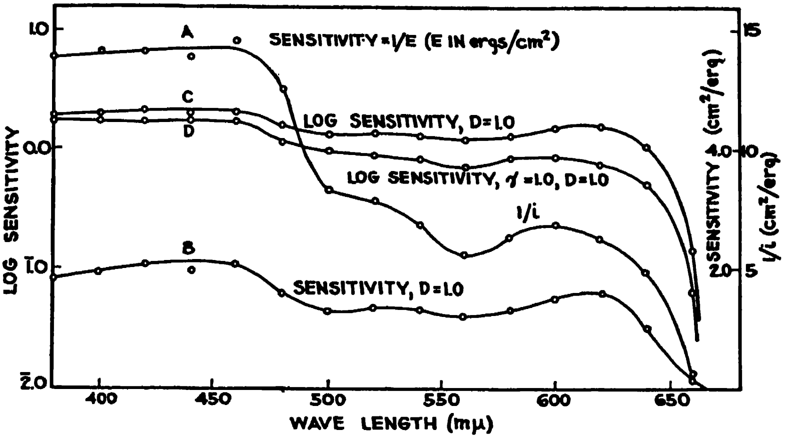

Fig. 202. Spectral sensitivity curves of panchromatic film expressed by various methods.

The van Kreveld addition law [11] furnishes a convenient method of calculating the sensitivity of an emulsion for any type of light source or combination filter and light source, provided the spec-

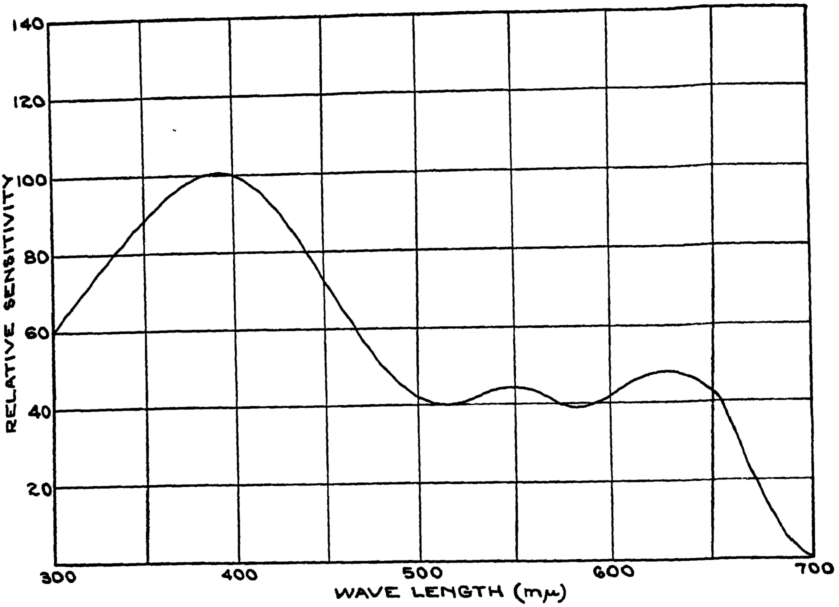

FIG. 203. Spectral sensitivity curve of panchromatic film plotted on an equal energy basis.

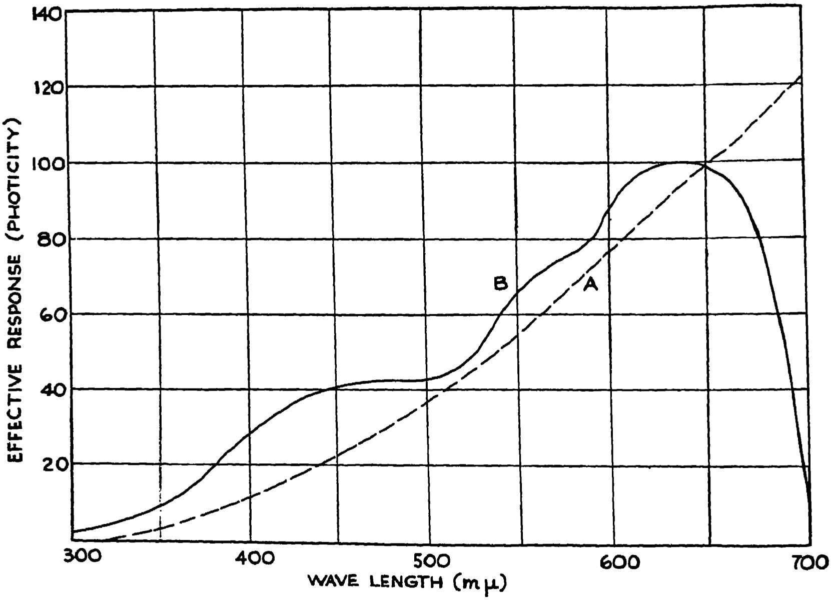

FIG. 204. *B*, spectral sensitivity curve of panchromatic film plotted as effective response to a lamp of energy distribution shown by curve *A*.

tral sensitivity data are available for the emulsion in question. A full description of it has been given by van Kreveld. (See also Chapters V, p. 224 and VI, p. 250.) The addition law may be stated as follows: If the energies required to produce a given density for a series of wave lengths, λ_1, λ_2, λ_3, etc., are, respectively, E_{λ_1}, E_{λ_2}, E_{λ_3}, etc., any combination of these wave lengths with combined energy, $\alpha E_{\lambda_1} + \beta E_{\lambda_2} + \gamma E_{\lambda_3} + \cdots$ etc., will produce the same density provided only that $\alpha + \beta + \gamma + \cdots = 1$. This law can be put into a more useful analytical form if the sensitivity of the emulsion, S_{λ_1}, to one wave length, λ_1, is expressed as the reciprocal energy, $\frac{1}{E_{\lambda_1}}$, required to produce the stated density. The sensitivity of the emulsion to any mixture of wave lengths, λ_1, λ_2, λ_3, etc., can then be expressed by the equation

$$S_m = \frac{a}{a + b + c + \cdots} S_{\lambda_1} + \frac{b}{a + b + c + \cdots} S_{\lambda_2} + \frac{c}{a + b + c + \cdots} S_{\lambda_3} + \cdots,$$

where a is the amount of energy of wave length λ_1 in the mixed radiation; b, that of wave length λ_2, etc.

If it is desired to express the sensitivity of the emulsion to a continuous band of wave lengths of energy distribution, $M(\lambda)$, the sensitivity to each wave length can be specified by $S(\lambda)$ and the above summation replaced by the integral

$$S_m = \frac{\int S(\lambda) M(\lambda) d\lambda}{\int M(\lambda) d\lambda}.$$

van Kreveld[12] has also shown how the above formula can be used to express the daylight sensitivity of an emulsion in terms of visual magnitudes. If $O(\lambda)$ is the spectral sensitivity function of the eye expressed in lux cm.^{2} sec./erg, the expression

$$S_l = \frac{S(\lambda) M(\lambda) d\lambda}{O(\lambda) M(\lambda) d\lambda}$$

can be considered as the daylight sensitivity in units lux^{-1} sec.$^{-1}$. Values of the quantity S_l for a number of emulsions are presented in the paper by van Kreveld mentioned above.

SPECTROGRAPHS

In spectrographs, the radiation from a suitable source is dispersed by means of a diffraction grating or prism, and the spectrum thus produced is allowed to fall directly upon the photographic material. The method has the advantages of simplicity and rapidity.

By control of the distribution of energy incident upon the entrance slit, the spectrograph may be made to give directly a graphic representation of the effective spectral response curve of the photographic material and light source used. Instruments of this kind are usually referred to as *wedge spectrographs*. A rotating sector of logarithmic form may be placed between the light source and the slit of the instrument.[13] Such rotating sectors, since they must be quite small, are rather difficult and expensive to manufacture; and a better solution of the problem is the use of a neutral gray wedge placed directly over the slit of the spectrograph, as proposed by Mees and Wratten.[14] The construction of such an instrument is shown in Figure 205. A diffraction grating provides normal dispersion. A scale plate is placed in the plate holder, so that during exposure a wavelength scale is printed directly on the spectrogram.

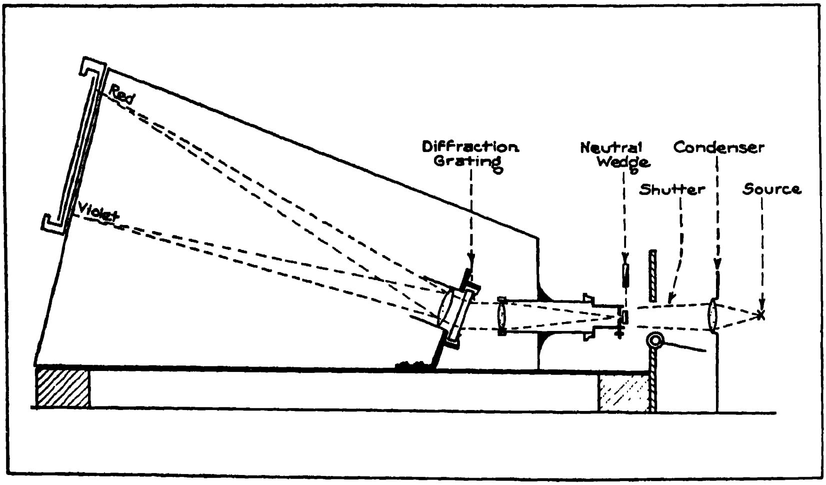

Fig. 205. Diagram of wedge spectrograph.

Various modifications of this instrument have been devised whereby spectrograms can be obtained for special types of energy distribution. A wedge spectrograph in which the photographic plate is exposed to a spectrum of uniform energy distribution gives directly the spectral sensitivity of the emulsion. An instrument designed to operate in this way has been described by Bertling.[15] In addition to the neutral wedge for modulating the intensity of exposure at each wave length, this instrument contains a neutral density near the focal plane of absorption, designed to bring the energy at each wave length to the same value. Another instrument, which was designed by Fricke [16] to give spectral sensitivity data directly, operates by having the photographic plate moved across the spectrum behind a slit and a movable wedge operated by a cam over the entrance slit. In this way, the intensity of the beam of light entering the instrument is controlled to give an equal energy exposure at each wave length.

Though wedge spectrographs giving equal energy exposures at each wave length are useful in special cases, by far their greatest field of application is in showing the response of a photographic plate to a given type of radiation source. For this purpose, the original type of instrument is quite suitable. In Figure 206 are shown examples of records obtained in the wedge spectrograph with photographic materials having various spectral sensitivities. The envelopes of the light portions constitute the spectral response curves for the various photographic materials as used with a particular light source. In the case illustrated, the quality of radiation was approximately equivalent to that of noon sunlight. It should be remembered in the interpretation of these spectrograms that the wedge used over the slit has a linear density gradient and, therefore, the distribution of radiation along the slit decreases logarithmically from one end to the other. These envelope curves, therefore, are in logarithmic form and cannot be compared directly with spectral sensitivity curves, such as that illustrated in Figure 203, where the ordinates are relative sensitivities, not the logarithms of sensitivity. The envelope curve represents, of course, the sensitivity indicated by the just perceptible extremity of the toe portion, as modified by the printing process, and not the inertia or unit density sensitivity. Two other facts should be kept in mind in judging these spectrograms. The apparent decrease in sensitivity at the short wave length end is due to selective absorption in the neutral gray glass of which the wedge is manufactured, and the wedge spectrograms made in this manner represent not only the spectral characteristic of the material but the spectral emission characteristic of the source used in the spectrograph.

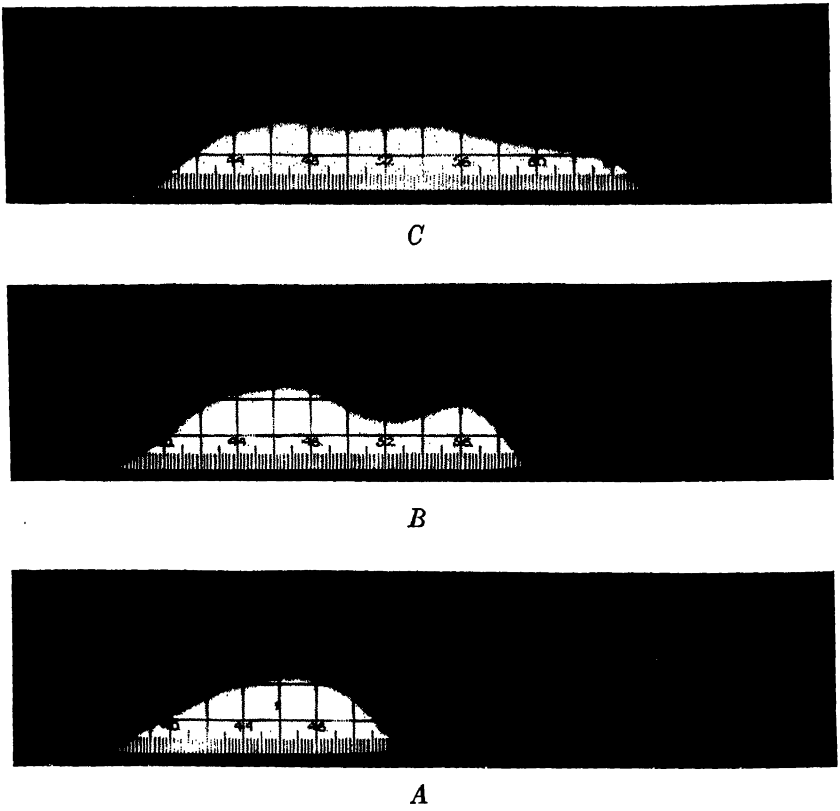

FIG. 206. Wedge spectrograms of (*A*) unsensitized, (*B*) orthochromatic, and (*C*) panchromatic materials.

It is possible to avoid the undesirable selective absorption characteristics of a neutral gray glass wedge by using a specially designed nonspherical condensing system for the illumination of the slit of the spectrograph. The various forms which have been proposed are discussed in Chapter XVI, p. 619, and are illustrated in Figure 170. Using such a system, Miller[17] designed a spectrograph with which the results illustrated in Figure 207 were obtained. This figure shows the spectrograms obtained on a panchromatic, an orthochromatic, and an ordinary (blue-sensitive) photographic material.

An inspection of wedge spectrograms yields a great deal of information as to the distribution of sensitivity and some qualitative idea of the variation in γ with wave length of the exposing radiation. They cannot be considered as satisfactory as the determinations made by monochromatic sensitometry, but as permanent, comparative records obtained without undue labor, wedge spectrograms have much to commend them.

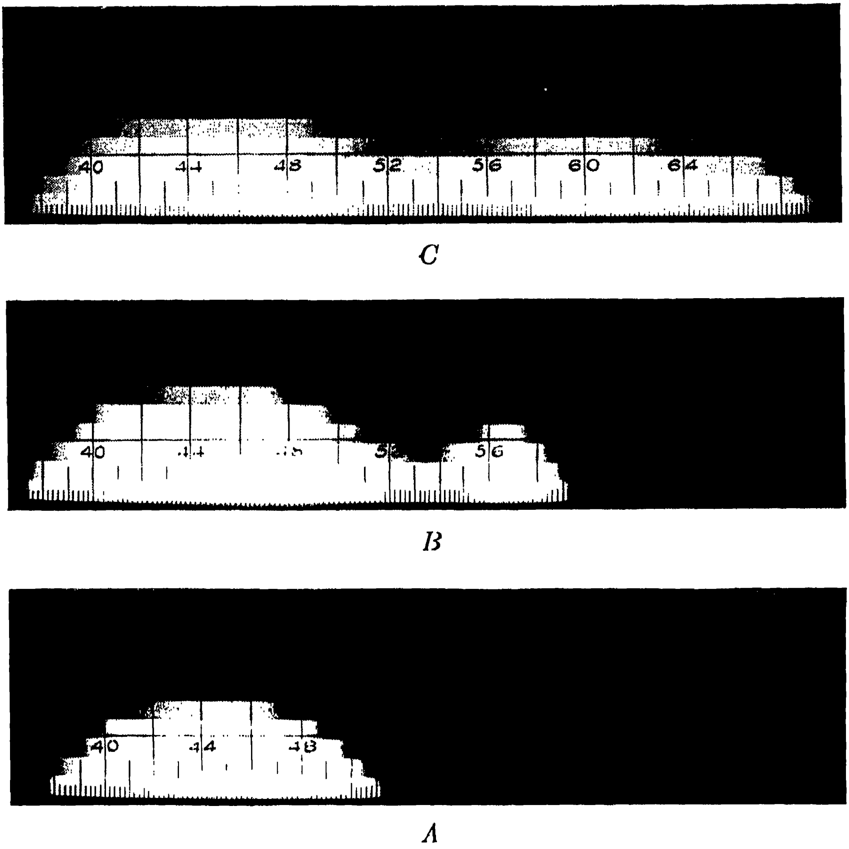

Fig. 207. Wedge spectrograms of (A) unsensitized, (B) orthochromatic, and (C) panchromatic materials taken on the Miller spectrograph.

To obtain a simple specification of color sensitivity expressed by a few numerical values, it is frequently convenient to depart from the monochromatic method and determine the response of photographic materials to relatively broad spectral bands. This method of obtaining a numerical expression for spectral sensitivity is very old, being used first about 1895,[18] probably by Abney. He used a tablet made of a series of colored glasses, each transmitting a relatively broad spectral band and adjusted to give equal illuminations. A similar method was used by Eder for testing the relative spectral sensitivity of orthochromatic plates. In his earlier work, the spectrum was divided into two parts: one containing all wave lengths longer than approximately 495 mμ; and the other, all wave lengths shorter than this. This wave length represents approximately the long wave length limit of the sensitivity of an ordinary noncolor-sensitized material. The values obtained, therefore, give the ratio between the sensitivity due to optical sensitizing and that due to the inherent sensitivity of the unsensitized silver halide. Later, Eder[19] divided the spectrum into three regions: orange-red,

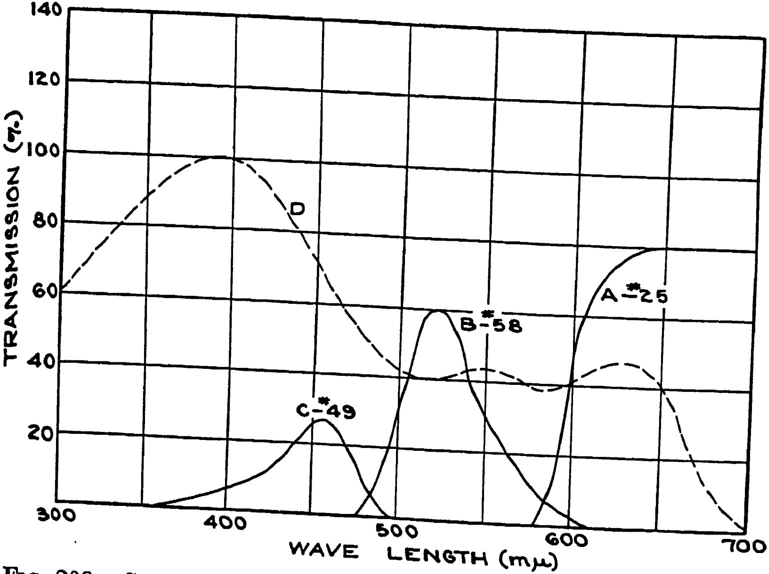

FIG. 208. Spectral transmission curves of Wratten filters; curve *D*, spectral sensitivity curve of panchromatic material.

green, and blue-violet. Wall[20] also employed three selectively absorbing filters, dividing the spectrum into three parts similar to those used by Eder.

Probably the most widely used method of this type involves the use of three filters having selective absorptions so adjusted as to divide the visible spectrum into three approximately equal wave-length bands. As typical of such filters, the Wratten tricolor set may be mentioned; and, in fact, since this set of filters is practically standard throughout the world for three-color processes, the expression of color sensitivity in terms of these three filters has become almost universal. In Figure 208 are plotted the spectral transmission curves of the three filters in question; namely, Wratten No. 25 (*A*), red; Wratten No. 58 (*B*), green; Wratten No. 49 (*C*4), blue.

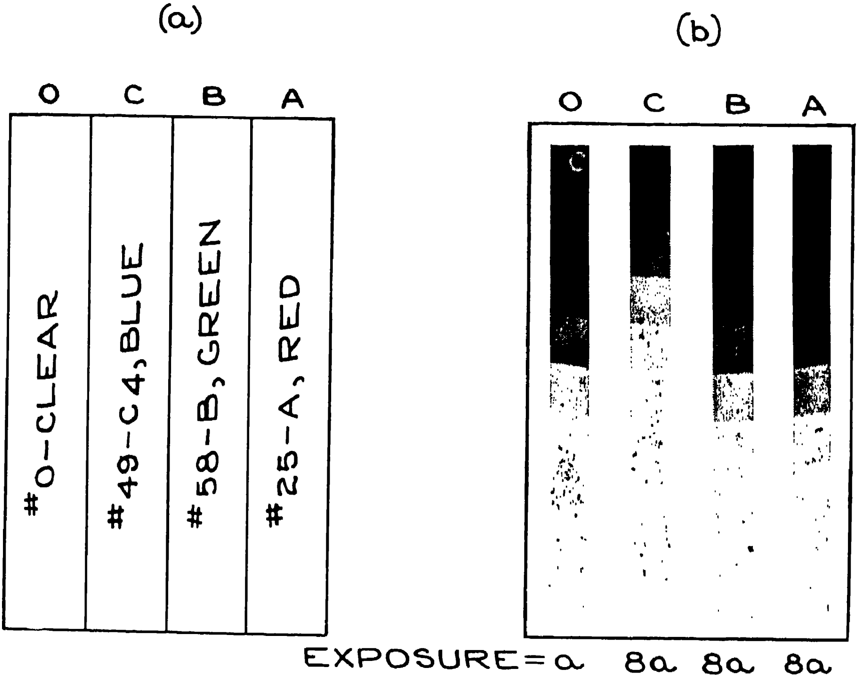

FIG. 209. Tricolor tablet for use in sensitometer.

In practice, sensitometric results are obtained by using a tricolor tablet of the structure illustrated at (*a*) in Figure 209. Strips of these filters, which are manufactured in the form of dyed gelatin, and a strip of undyed gelatin film are cemented between two sheets of glass. The dimensions of this tablet are such that it just fits into the plate holder of a sensitometer of the ordinary *white-light* type, and the strips are of such width that one sensitometric exposure is made through each of the four filters. To obtain exposures through the tricolor filters which balance fairly well with that made through the clear filter, it is customary to increase the time of the tricolor filter exposures so that it is eight times as long as that made through the clear area. At (*b*), Figure 209, is shown the result obtained by application of this method to a panchromatic material. The result is expressed usually in terms of the *filter factors* for the tricolor filters, these being the factors by which the exposure without a filter must be increased to give the same result when the filters are interposed. These factors are an expression of the color sensitivity of the material. Thus, in Figure 208, the dotted curve *D* is the spectral sensitivity curve of the panchromatic material used in making the tricolor exposure reproduced at (*b*) in Figure 209. The tricolor ratio for this material, estimated by use of the densities in the half-tone region, is 16–8–6, these numbers being, as mentioned previously, the multiplying factors for the blue, green, and red filters, respectively. This conveys some idea of the relation between the spectral sensitivity of a photographic material expressed in terms of the sensitivity-wave length function, as derived by the methods of monochromatic sensitometry, and the tricolor ratio values.

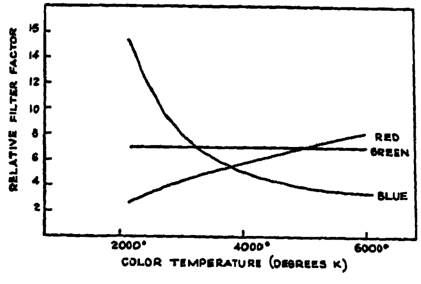

Fig. 210. Effect of the color temperature of the source upon filter factors.

The filter factors depend, of course, upon the color of the light source. If they are to be used in practical photography, they must be determined for the light source with which they are to be employed. The variation of the filter factors with the color temperature of the light source is illustrated in Figure 210, in which the relative filter factors for the three Wratten filters are plotted against the color temperature of the light source.

The filter factors vary also with the way in which the material is developed. Thus, if they are to be used in making separation negatives, for example, and the three negatives are to be developed to get the same γ, then the filter factors will be proportional simply to the inertia readings derived from the characteristic curves. On the other hand, if the three exposures behind the filters are on the same film or are otherwise developed together for the same time, they will have somewhat different values of γ, and the filter factor will depend upon the density at which the exposures are to be matched. Thus, in Figure 211 are shown the characteristic curves for unfiltered, red, green, and blue exposures on Eastman Tri-X Panchromatic film, and from these curves the following table can be constructed:

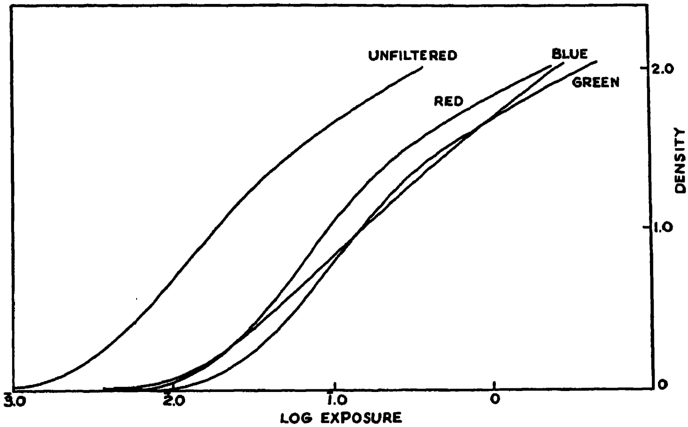

FIG. 211. Characteristic curves of panchromatic film exposed through filters.

FILTER FACTORS

D	*Red*	*Green*	*Blue*
0.5	5.5	8.3	6.3
1.0	5.0	7.8	8.1
1.5	4.8	8.5	9.5
2.0	6.6	11.0	7.4

It is seen that when the negatives are developed for the same time, different factors are required, according to whether the match of density is to be obtained in the highlights or in the shadows. The relative γ's obtained depend upon the time of development, so that the relative filter factors also depend upon the time of development. The γ-wave length curves for a series of development times which apply to a particular panchromatic material are shown in Figure 212.

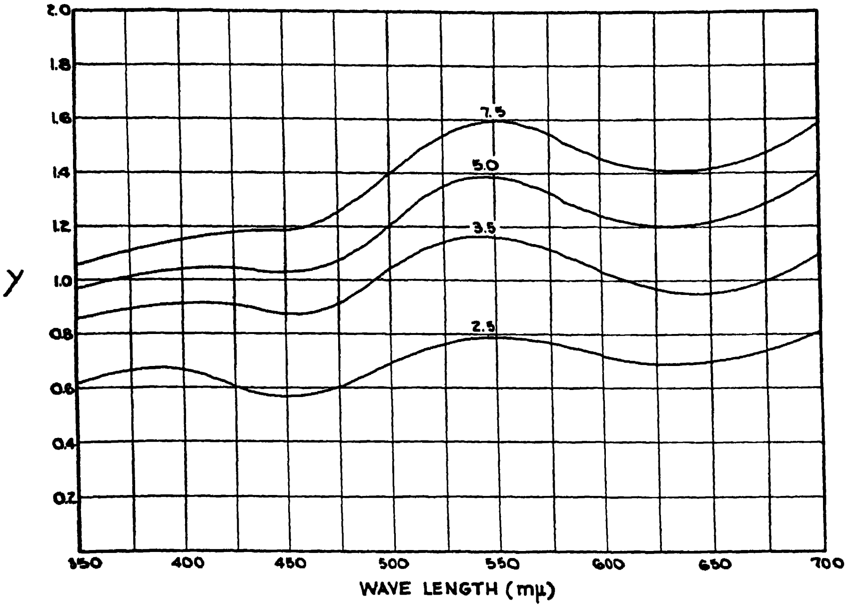

FIG. 212. γ, wave length curves for a series of development times.

The relative filter factors also depend upon the reciprocity law failure of the material. This can be seen from Figure 213, in which the reciprocity curves show the exposure required to produce a density of 0.50 over a wide range of exposure times for light passing through the red, green, and blue filters on a typical panchromatic material. The lines of constant time are vertical, and the constant intensity lines are at 45° to the log time axis. It is seen that the filter curves are parallel to the non-filter curve since the reciprocity law failure is independent of the color of the light. The log It separation of the filter curves and the non-filter curve is equal to the effective absorption of the filters. Since the vertical separation of these curves is identical anywhere along the log-time axis and since vertical separations represent exposure ratios for equal photographic effect at constant *time* and variable *intensity*, it is apparent that the exposure ratios, or filter factors, will be constant only when exposure is increased by increasing the intensity of the filtered light. On the other hand, the amount by which exposure must be increased by increasing the exposure *time* rather than *intensity* is represented by the log It separation of the constant intensity intercepts of the reciprocity curves. The magnitude of this separation is dependent upon the intensity level at which the constant intensity line is drawn and, therefore, the filter factors applied in this manner depend upon the reciprocity law failure of the material. Thus, in Figure 213, when the exposure time is 1/10 second for the non-filter exposure, the variable *intensity* filter factor for the blue filter is represented by the log It separation of the blue and non-filter curves along line MN and the variable *time* factor by the log It separation between M and O. These factors are 17 and 16, respectively. If the non-filter exposure time is 10 seconds instead of 1/10 second, the variable *intensity* factor, as measured at AB, is again 17; but the variable *time* factor, represented by the log It separation between A and C, is now 47. In practice, therefore, filter factors must be determined for the conditions in which they are used.

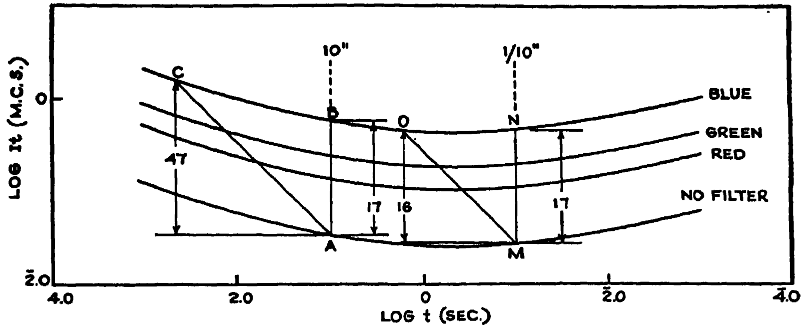

FIG. 213. Reciprocity curves for panchromatic material exposed through filters.

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CHAPTER XIX

THE INTERPRETATION OF SENSITOMETRIC RESULTS

In the practice of sensitometry, the photographic material is exposed to a known quantity and quality of radiation, is developed under standard conditions, and the densities resulting from the various exposures are then measured. The results are expressed in graphic form by plotting curves, and from these curves numerical constants are derived which are used in specifying the characteristics of the material.

The most generally used curve is in the form proposed by Hurter and Driffield for the presentation of sensitometric data, in which the density is plotted against the logarithm of the exposure.* This is properly called the *characteristic curve*, but it is more popularly known as the *H and D curve*. For the purposes of this discussion, a typical curve is shown in Figure 214. According to the mathematical formulas, the characteristic curve should have a definite inflection point, but in practice a considerable portion of the $D, \log E$ curve of negative materials is a straight line within the limit of experimental error, and the attainment of more precise data by refinement of sensitometric methods does not result in showing any deviation from a straight line for many actual materials, so that the theoretical inflection point cannot be determined experimentally with precision. Throughout the straight-line portion of the characteristic curve, the density is directly proportional to the logarithm of the exposure, and for the correct proportional rendering in the negative of the various object brightnesses, the camera exposure should be adjusted so that the brightnesses to be rendered fall in the straight-line region of the curve.

The relation between a given $\log E$ interval, $\Delta \log E$, and the corresponding density interval, ΔD, is given by the ratio $\frac{\Delta D}{\Delta \log E}$, which is an expression of the average slope or gradient G for the interval $\Delta \log E$. Except for the straight-line portion of the curve, the gradient is not constant and must be expressed generally in the differential form, $G = \frac{dD}{d \log E}$. For the straight-line portion, however, the gradient is constant and can be expressed as the tangent of the angle α formed between the straight-line portion of the characteristic curve and the $\log E$ axis. The tangent of this angle was called *gamma*, γ, by Hurter and Driffield. For the straight-line portion, therefore,

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* See also Chapter V, p. 201, Chapter XI, p. 402, Chapter XVII, p. 638, and especially Chapter XVI, p. 589, in which some of this discussion is necessarily duplicated.

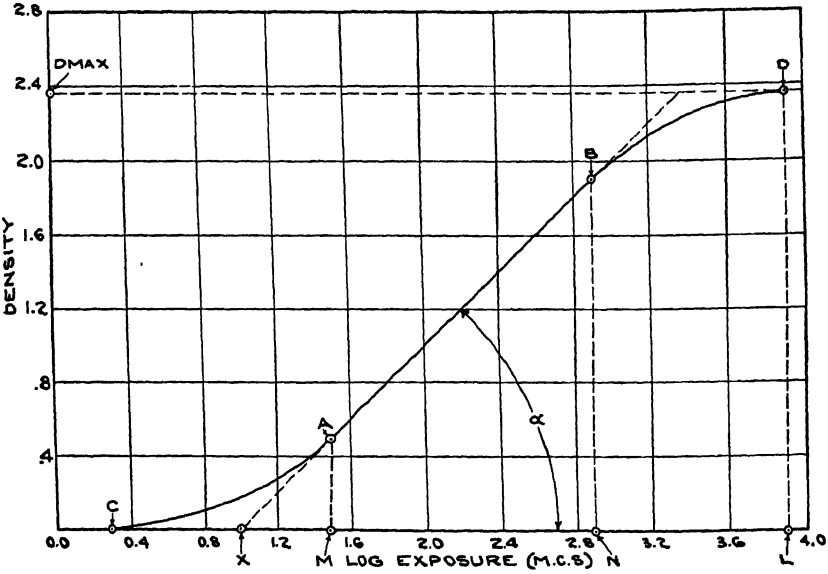

FIG. 214. The characteristic curve of Hurter and Driffield.

$$G = \frac{dD}{d \log E} = \text{constant} = \tan \alpha = \gamma.$$

Thus, γ is the proportionality factor giving the relation between a given $\log E$ difference, $\Delta \log E$, and the corresponding density difference, ΔD:

$$\Delta D / \Delta \log E = \gamma.$$

If, in an object being photographed, two areas have brightnesses of 10 and 80 units, the $\Delta \log E$ value becomes $\log 80 - \log 10 = 0.90$. If both are rendered on the straight-line portion of the D log E curve and if $\gamma = 0.8$, then

$$\Delta D/0.90 = 0.8$$

and

$$\Delta D = 0.72.$$

If $\alpha = 45°$, tan α or γ becomes unity, and any log E increment is rendered in the negative by an identical density difference. This is the condition which must be fulfilled if it is desired to reproduce exactly in the negative the brightness contrast in the object. If γ is less than unity, correct proportional reproduction will be obtained but with compression of the object brightness scale, while, if γ is greater than unity, correct proportional reproduction will also be obtained but with expansion of the brightness scale.

Since γ is equal to the ratio of the negative density difference to the corresponding log exposure difference, it is frequently used as a means of expressing the contrast of the negative or of the photographic material. It should be borne in mind constantly that γ gives information pertaining only to the straight-line portion of the curve and tells nothing of the contrast characteristics of other portions of the D, log E curve.

Projection of the straight-line portion of the D, log E curve on the log E axis determines the log exposure range over which direct proportionality between D and log E exists. By dropping perpendiculars from A and B (Figure 214) to the log E axis, the points M and N are established. These fix the limits of this exposure range. The distance between M and N is called *latitude*, and may be expressed either in log E units or in exposure units. Thus,

$$\text{Latitude} = \log E_N - \log E_M \text{ (log } E \text{ units)}$$

or

$$\text{Latitude} = E_N/E_M \text{ (exposure units).}$$

The value of latitude for any given D, log E curve determines the maximum object contrast (ratio of maximum to minimum object brightness) which may be rendered with strict proportionality between density and log exposure on that photographic material processed under the specified conditions used in obtaining the characteristic curve. Latitude is not a constant for a given photographic material, since its value depends upon the extent to which development is carried and, to a lesser extent, on other processing factors. It depends also upon certain exposure conditions, such as the quality (spectral composition) of the exposing radiation.

When the straight line is produced to cut the axis, the point x at which the intersection occurs was called by Hurter and Driffield the *inertia*, i. They utilized this point as a measure of the sensitivity of the photographic material, taking the sensitivity as proportional to the reciprocal of the inertia and expressing the effective sensitivity or *speed* of the material as equal to a constant divided by the inertia,

$$S = \frac{k}{i}.$$

From the point A (Figure 214) the D, $\log E$ curve continues to the left into the region of decreasing exposure with constantly decreasing gradient, G, until at the point C this gradient becomes zero; that is, the curve becomes parallel to or, if correction for fog has been made, coincident with the $\log E$ axis. This region, C to A, may be referred to as the *toe* of the characteristic curve. Since the gradient, $\frac{dD}{d \log E}$, decreases progressively from A to C, it follows that the density difference, ΔD, corresponding to a given small $\Delta \log E$, decreases continuously as the exposure is decreased, becoming zero at the exposure value corresponding to the point C. Thus, the power of the photographic material to show detail due to brightness differences in the object becomes less and less through the toe of the curve, vanishing entirely at an exposure value corresponding to the point C.

From the point B, the upper limit of the straight line, the curve continues to the right into the region of increasing exposure with a constantly decreasing gradient until, at the point D, the gradient becomes zero, that is, the curve becomes parallel to the $\log E$ axis. The value of density corresponding to the point D is the *maximum density*, $D_{\max}$, obtainable with the specified processing conditions, development time, developer constitution, temperature, etc. This region, B to D, is called the *shoulder* of the characteristic curve. Here, the density difference, ΔD, corresponding to a small $\log E$ difference, $\Delta \log E$, decreases progressively with increasing exposure and becomes zero at point D. Thus, the detail-rendering power decreases progressively with increasing exposure and vanishes completely at the exposure value corresponding to point D.

Points C and D, therefore, represent the limits of the exposure range within which the material is capable of rendering an object brightness difference by some density difference, although near the limits (points C and D) this may be negligibly small, even for very great object brightness differences. This exposure range is termed the *total scale* of the material and may be expressed either in $\log E$ units or as the ratio of the limiting exposures. Thus,

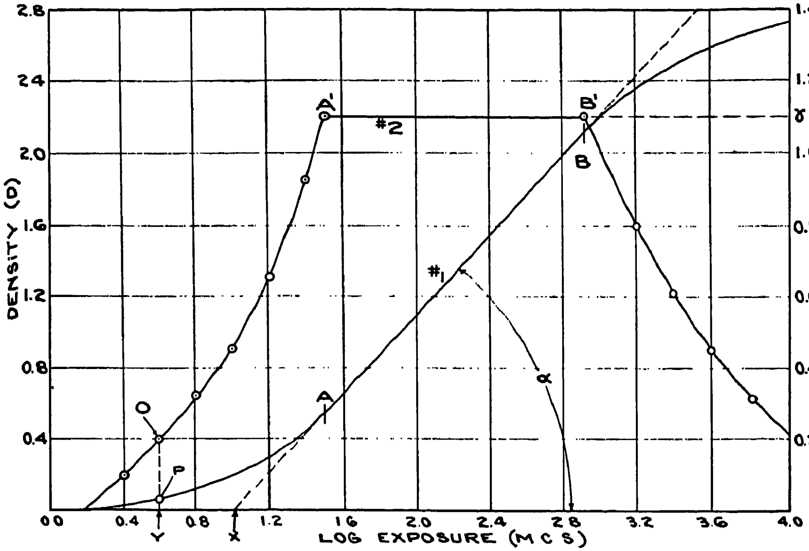

FIG. 215. Derivative of the characteristic curve.

$$\text{Total scale} = \log E_L - \log E_C \ (\log E \text{ units})$$

or

$$\text{Total scale} = \frac{E_L}{E_C} \ (\text{exposure units}).$$

The gradient of the characteristic curve is of such importance, especially in connection with the problems of tone reproduction, that it is often desirable to use a derivative curve. In Figure 215, the curve marked No. 1 is the usual characteristic curve obtained by plotting D against $\log E$, while that marked No. 2 is its derivative, obtained by plotting $\frac{dD}{d \log E}$ as a function of $\log E$. This curve shows clearly the way in which gradient changes with log exposure. For the straight-line portion of the curve lying between points A and B, gradient is constant and equal to γ. The first derivative curve throughout this region is a straight line parallel to the $\log E$ axis and having an ordinate value equivalent to γ, as shown on the gradient scale at the right of the figure. For values of exposure less than A and greater than B, the first derivative curve takes the form shown. This graphic form is useful where it is desired to determine precisely the exposure value corresponding to some particular slope of the $D, \log E$ curve. It contains no more information nor can it be drawn with any greater precision than the $D, \log E$ curve itself, but for many purposes it presents the data in more convenient form and gives a more vivid mental picture of the relation between gradient and exposure.

The shape and position of the characteristic curve depend upon the conditions of development. The relation between the time of development and the value of γ was dealt with in Chapter XI. The increase of γ can be seen in Figure 216, which shows a group of characteristic curves obtained for increasing times of development. The corresponding γ, t curve is shown as an insert. These γ, t curves are often of great value in analyzing the characteristics of a photographic material and are prepared from the sensitometric data obtained by developing exposed strips for a series of different times, plotting the characteristic curves and then plotting the γ values derived from these curves against the time of development. The measured densities may either be plotted directly against the logarithms of the exposures to obtain the characteristic curve, or the values of fog and of base density may be subtracted. The fog is determined by measuring the density of an area on the photographic material which has received no exposure but which has been developed. For most photographic materials, the value of fog is relatively low for the shorter development times but usually grows at an increasing rate as the development time is extended. Any value of fog which is given for a photographic material obviously must be accompanied by some specification of the development time or the extent of development (in terms of γ) in order to have any definite significance. The t_d, fog curve is, of course, a complete representation of the relation between fog and the extent of development and should be used where possible instead of attempting to express this factor by a single numerical value.

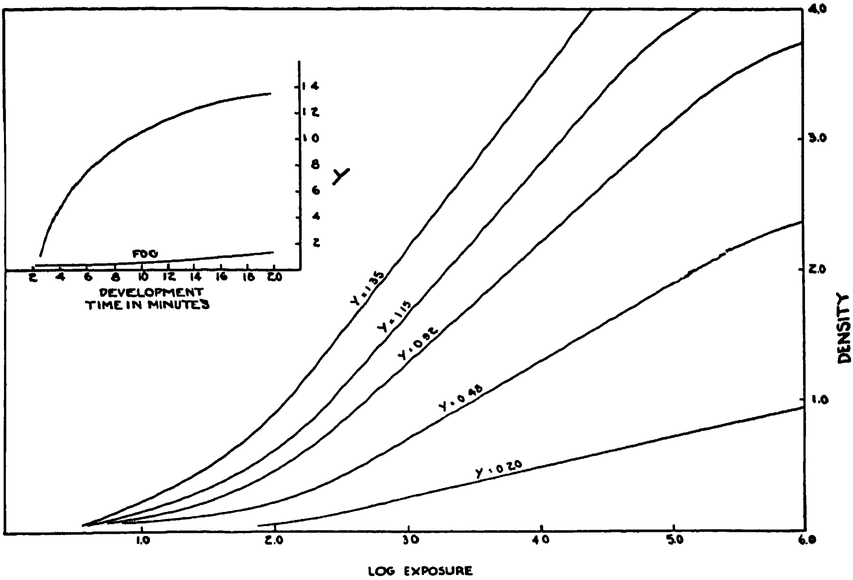

FIG. 216. Family of characteristic curves with corresponding γ, t and fog, t curves.

In the practical presentation of sensitometric data, a convenient form is to prepare a complete family of D, $\log E$ curves obtained with various development times; these, together with a γ, t curve and a time, fog curve, serve as a fairly satisfactory graphic representation of the sensitometric characteristics. In Figure 216 is illustrated one way in which these various functions may be conveniently shown together. The characteristic curves themselves are drawn in, and the value of γ for each is indicated. In the upper left-hand portion of the rectangle are shown the γ, t and time, fog curves derived from the D, $\log E$ curves. The curves shown in Figure 216 apply to a high-speed negative material for which γ_∞ is relatively low, being of the order of 1.4 to 1.5 as indicated by extrapolation of the γ, t curve.

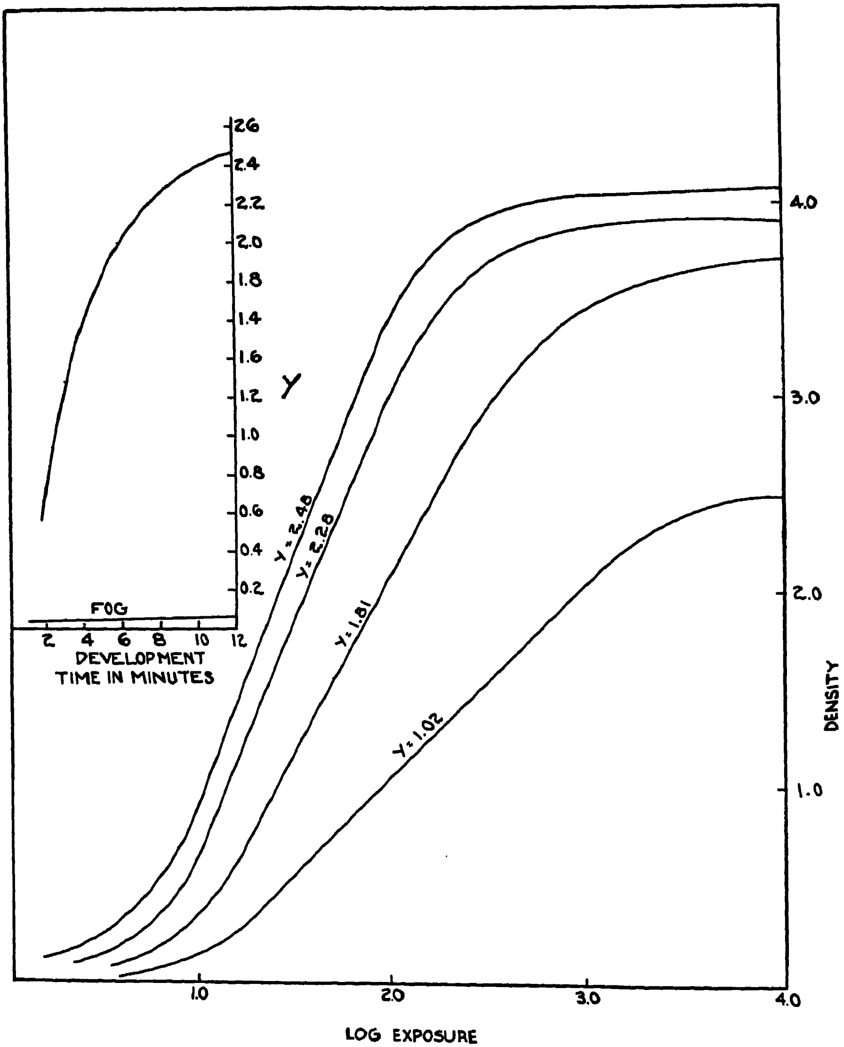

FIG. 217. Family of characteristic curves for motion-picture positive film.

In Figure 217 is shown a similar group of curves for motion-picture positive film, which is a relatively slow, high-contrast material.

THE DETERMINATION OF SENSITIVITY

The primary purpose of sensitometry is the measurement of the sensitivity of photographic materials in order to expose them quantitatively, so that a definite, desired result may be achieved. In the early work on photographic sensitometry, great emphasis was placed upon this purpose, and it was the objective of Hurter and Driffield when they started their classic work on the response of photographic materials to light.

In all photography, the effective sensitivity of a photographic material depends upon the result which is required and the exact way in which it is used. Thus, in astronomical photography, quite different sensitometric measurements are required from those utilized in pictorial photography. One great difference is, of course, the intensity level at which the exposure is made. In astronomical photography, exposures of minutes and hours are common, while in the use of the ordinary camera, exposures are timed in fractions of seconds. The relative sensitivity of photographic materials is not constant for different intensity levels (Chapter VI), and in astronomical photography it is necessary to measure the sensitivity of the materials at intensity levels very different from those which are employed if the results are to be applied in pictorial work.

TABLE LXVIII

Speed Numbers at Different Exposure Levels

	Camera Level $I = 20$ *M.C.*		*Spectroscopic Level* $I = 0.1$ *M.C.*		*Astronomical Level* $I = 0.0001$ *M.C.*	
	$10/i$	S_A	$10/i$	S_A	$10/i$	S_A
Eastman 50	670	14	710	16	190	5.6
Eastman 40	520	14	820	23	370	12
Eastman 33	220	9	380	12	120	3.6
Eastman Process	60	3.5	50	2.9	19	1.0
Type 103 0	1240	56	980	72	540	34
Type I 0	890	35	1120	46	280	14
Type II 0	210	17	250	20	95	6.8
Type III-0	140	8.5	100	6.3	35	2
Type IV-0	50	3.3	50	3.0	30	1.9
Type 144 0	40	2.9	35	2.5	25	1.8
Type V-0	0.4	0.03	0.3	0.02	—	—

In Table LXVIII are given the speed numbers for a number of different plates used in astronomical and spectroscopic photography at three different levels of intensity—the camera level, which is taken as 20 meter candles; the spectroscopic level, with an intensity of 0.1 meter candle and an effective exposure of a few seconds; and the astronomical level with an intensity of 0.0001 meter candle, corresponding to an exposure time of the order of an hour. The values are given in two different scales, of which the $\frac{10}{i}$ scale is inversely proportional to the inertia and is found by dividing that value into 10, while the S_A value is obtained as follows:

Consider the characteristic curves of two materials, *A* and *B*, shown in Figure 218. If the speed is measured in terms of inertia, *A* is a faster plate than *B*. This is true also if sensitivity is judged by the exposure required to produce a minimum deposit. If, therefore, the purpose is to obtain a faint image with the shortest possible exposure, material *A* is selected. If, on the other hand, a certain minimum density in the image is required in order to make satisfactory readings on the plate and this density is supposed to be a value above that of the intersection point of the two curves, then, *for that purpose*, *B* is a faster material than *A*. According to Dunham,[1]

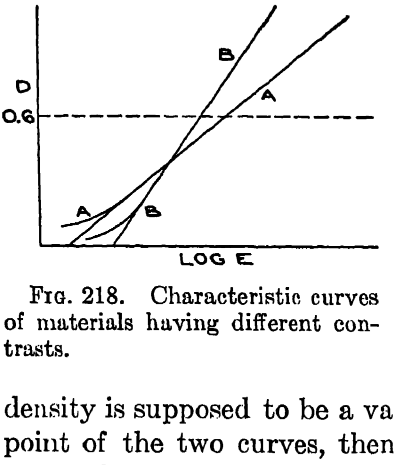

FIG. 218. Characteristic curves of materials having different contrasts.

> "In photographing stellar spectra what is required is a certain minimum density of about 0.6, which is adequate for the detection and measurement of weak absorption lines."

Naturally, the determination of the exposure required to produce a given density involves a decision as to the γ which it is practicable to reach in development. Consideration of this question seems to indicate that in practice the maximum γ to which plates can be developed as a routine with a minimum of fog may be taken as 80 per cent of γ_∞. Accepting Dunham's criterion, then, the astronomical sensitivity S_A may be defined as inversely proportional to the exposure expressed in seconds at one meter to one candle power of the international high-temperature standard light source which will produce a density of 0.6 when the material is developed until γ reaches a value of 0.8 γ_∞. As in the case of the inertia values, the S_A values depend upon the intensity level in order to provide for the varying reciprocity failure of the materials. A comparison of the relative effective speed of two of the materials shown in the table will show that, using $\frac{10}{i}$ values at the camera level, "Type 103–0" is given a speed 1.85 times that of "Eastman 50," while at the astronomical level, using S_A values, "Type 103–0" is 6.2 times that of "Eastman 50."

A case where a special method of determining effective speed is required is that which occurs in the making of line and half-tone negatives for photoengraving, where there is no scale of gradation to render. There are only two tones in an ideal process negative—clear glass and opaque deposits. In half-tone negatives, the gradation is rendered by various *sizes* of dots and not by various densities. This being so, a plate which will give the necessary opacity to the highlights of a line negative or the dots of a half-tone negative with less exposure than another plate is effectively faster, without regard to any question of gradation. To put the matter in another way: If two plates have curves with straight-line portions that meet the exposure axis at the same point and one can be developed to give more contrast than the other, then the plate which gives greater contrast is effectively faster when used for line or half-tone negatives.

It will be seen that in order that speed ratings of negative materials should have real value for the control of exposures in the camera, they should be determined in the laboratory under conditions corresponding as exactly as possible to those which occur when they are used. The light should be of the same quality and approximately the same intensity as that which forms the camera image, the modulation of the exposure should be by the intensity of the light and not on a time scale, the time of exposure should be of the same order as that used in the camera, and the criterion of exposure should be that by which practical exposures are judged. Sensitometric methods have approximated these requirements more and more closely as they have been improved and now fulfill them with satisfactory accuracy.

One of the earliest methods used for the expression of sensitivity was to specify the exposure required to produce a just perceptible density (Chapter XVI). The earliest standard sensitometer, in fact, was Warnerke's tablet adopted by the committee of the Photographic Club of London in 1881, and this method was also used in the Scheiner instrument and the Eder-Hecht sensitometer. What is effectively a modification of this system is the *DIN* system (Chapter XVI, p. 592), adopted in Germany in 1931, in which the speed is derived from the exposure required to produce a density of 0.1 above the fog level.

Hurter and Driffield used the numerical values of inertia obtained from their characteristic curves for the computation of the speed of the photographic plates which they used. The selection of the inertia point by Hurter and Driffield was derived from considerations relating to the correct reproduction of tone in the negative. In order that the scale of brightness existing in the object may be represented correctly in the negative, it is necessary that the exposures representing those brightnesses should fall upon the straight-line portion of the characteristic curve and thus that the minimum exposure given should not be less than that which corresponds to point A in Figure 214, while the exposure for the brightest object must not be greater than that which corresponds to point B. Using this criterion for correct exposure, in which the entire scale is reproduced upon the straight-line portion of the characteristic curve, it follows that the effective sensitivity of the material is inversely proportional to the inertia point—where the extension of the straight-line portion of the curve cuts the log E axis.

Granting the assumptions as to the necessity for correct reproduction of the tones in the negative, the inertia value is a correct indication of the speed. As will be shown later, however, the general consideration of tone reproduction has led to other conclusions than those reached by Hurter and Driffield, since the effective exposure required for best reproduction in the final print is not dependent alone upon the characteristic of the negative material but also upon the characteristic of the printing material.

Hurter and Driffield obtained the speed number used in their actinograph by dividing the inertia into 34, which gave a series of speed values of convenient magnitude for practical use. The Watkins speed scale is also based upon inertia, but, instead of using 34, as suggested by Hurter and Driffield, Watkins adopted 68.[2] The actual relation between the Watkins and *H* and *D* numbers, however, indicates that the Watkins constant is more nearly 50 than 68.[3] In the fourth column of Table LXIX are shown the values of the Watkins speed scale in comparison with the other well-known systems.

TABLE LXIX

RELATIVE SPEED NUMBERS

Scheiner	*Eder-Hecht*	*H and D*	*Watkins*	*Wynne*	*Relative*
1	42	7	11	*F*/21	1
2	46	9	13	*F*/24	1.27
3	48	12	17	*F*/21	1.62
4	50	15	22	*F*/30	2.07
5	53	19	28	*F*/34	2.64
6	56	24	36	*F*/38	3.36
7	58	31	45	*F*/43	4.28
8	61	40	58	*F*/49	5.45
9	64	50	74	*F*/55	6.95
10	66	64	94	*F*/63	8.86
11	68	82	122	*F*/71	11.3
12	71	104	153	*F*/79	14.4
13	74	133	196	*F*/90	18.3
14	77	170	250	*F*/101	23.4
15	80	216	317	*F*/114	29.8
16	82	276	405	*F*/129	37.9
17	84	351	515	*F*/145	48.3
18	86	448	660	*F*/165	61.6
19	88	570	840	*F*/196	78.5
20	90	727	1065	*F*/209	100.0

The obsolete Wynne[4] numbers in the fifth column are the products of 6.4 and the square root of the Watkins number.

With the introduction of photoelectric exposure meters, various *speed rating numbers* have been adopted by their makers. The Weston numbers are derived from the inertia and are expressed as inversely proportional to the exposure required to give a density numerically equal to the γ obtained in development. Thus, if E_w is the exposure required to give $D = \gamma$, the Weston rating number is $4/E_w$.

For many purposes and under many conditions, the expression of speed in terms of inertia is of great value. So long as all of the straight-line portions of a family of D, log E curves pass through a common intersection point and this point lies on the log E axis, *inertia* and hence *speed* are independent of development time. Under such conditions, the speed becomes a very significant constant for the photographic material. Unfortunately, practical developers do not generally give a common intersection point which lies upon the log E axis; in the presence of free bromide, whether in the developing solution or the photographic material itself, the intersection point is depressed to a position below the log E axis. This is shown in Figure 108 on p. 412, where the depression of density by bromide is discussed. Under such a condition, it is evident that the inertia will vary with the γ and a speed value derived from the inertia will only be significant for a given degree of development and, correspondingly, a given γ value.

The extent of the dependence of the inertia speed upon γ is illustrated in Table LXX. These data are derived from measurements made on a high-speed negative material processed in a developing solution containing some bromide. The straight-line portions of the D, log E curves intersect at a point well below the log E axis. The development times, T_d, extend from 3 to 20 minutes, the corresponding γ range being from 0.27 to 1.12. For this range in development, the reciprocal inertia changes from 22 to 140, a sixfold increase in speed as derived from inertia values.

TABLE LXX

INCREASE OF SPEED WITH DEVELOPMENT TIME AND γ

T_d	γ	i	$1/i$
3	0.27	0.045	22
5	0.43	0.020	50
8	0.68	0.012	82
12	0.83	0.010	100
20	1.12	0.007	140

The complication involved in expressing speed by means of the inertia does not end here. Many materials exist for which there is no single point of intersection for the straight-line portions of the D, log E characteristics. Some materials do not give very satisfactory straight-line relations between density and log exposure. There is wide divergence in the relative shape of the underexposure regions and, in fact, an almost endless variety of conditions is found, which makes it difficult to generalize satisfactorily the expression of practical or effective speed from the characteristic curve. Anomalous behavior in both shape and position of the D, log E curves resulting from development for different times seems to be particularly common in materials of high sensitivity. This subject has been discussed by Sheppard.[5] He classifies emulsions generally into *orthophotic* and *anorthophotic* categories. Orthophotic materials show a definite convergence point of the straight-line portion of the characteristic curves, while anorthophotic materials depart from this condition, showing no tendency to give a common point of convergence. Sheppard concludes from his study of the subject that emulsions of the anorthophotic type have characteristics which are much less reproducible from batch to batch than those of the orthophotic class.

The chief function of a photographic negative material as used in practice is to reproduce as density differences the brightness differences existing in the object photographed. The minimum useful exposure, therefore, will be that required to reproduce the brightness difference existing in the shadow regions of the object with some minimum contrast, and following this reasoning it seems logical to require that the minimum useful exposure should be determined as that necessary to obtain some specified gradient of the characteristic curve; that is, it is the exposure at which $\frac{dD}{d \log E}$ has some specified value. This idea was discussed by Luther[6] and further developed by Jones and Russell.[7] The difficulty in carrying it out is that of deciding upon the value which is to be taken as representing the minimum useful gradient. It has been suggested that this value should be 0.5. Judging from data available in publications by Goldberg[8] and discussed in a paper by Jones[9] dealing with the contrast of photographic printing papers, it appears that this value is too high and that satisfactory reproduction of object detail can be obtained by utilizing portions of the characteristic curve of lower gradient. The subject has also been discussed by Sheppard,[5] who states that the minimum useful gradient "will in general depend not only upon the negative but also upon the positive aspect of tone reproduction so that its fixation is not expressible by a unique function of the negative material itself." This conclusion is undoubtedly correct, and its validity is supported by the data and the discussion given by Jones.

It seems quite possible for certain definite classes of work to establish a value of minimum negative gradient in terms of which sensitivity or speed may be expressed usefully. For instance, from a knowledge of common practice in motion-picture photography, it is possible to draw fairly definite conclusions as to the minimum useful gradient of negative materials used in this work. This knowledge is based upon densitometric analyses of a large number of motion-picture negatives and positives. The minimum gradient indicated lies between 0.1 and 0.3. A similar value is known to represent fairly well the conditions existing in amateur photography.

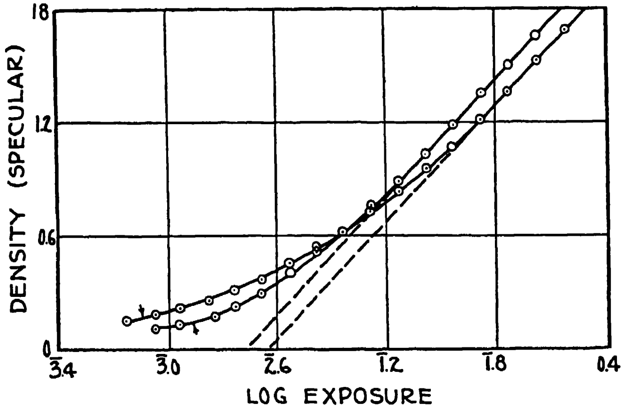

FIG. 219. Characteristic curves of different shapes from materials developed to the same γ.

A typical case which illustrates the merits of this method of expressing speed is shown in Figure 219. The two materials illustrated have been developed to the same γ; and, on the basis of the inertia method of expressing speed, the material of which the straight-line portion cuts the log E axis farthest to the left has the higher speed of the two. The small arrows indicate the points on the underexposure region where G is equal to 0.2. It will be seen that the minimum limiting gradient method reverses the speeds of the two materials. If inertia speed is expressed as 10 times the reciprocal of the inertia and the gradient speed as 10 times the reciprocal of E_m, the numerical results derived from Figure 219 are as follows:

	$10/i$	$10/E_m$
A	220	1360
B	269	720

A further illustration of this suggested method is given in Figure 220, in which are shown the underexposure regions of four

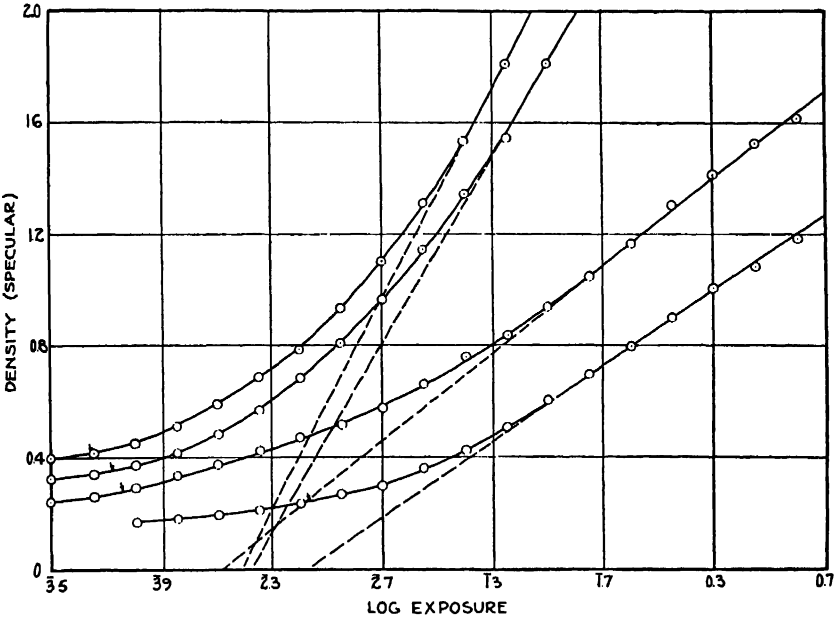

FIG. 220. Variation of exposure corresponding to minimum gradient with development.

D, log E characteristic curves obtained by using different times of development. Again, the points of gradient equal to 0.2 are indicated by the small arrows attached to each curve. In the case of the shortest time of development, it will be noted that the gradient for 0.2 is obtained for an exposure value practically equal to the inertia value, while for longer times of development the speed values based upon minimum gradient are very much higher than those based upon inertia. The data corresponding to the curves in Figure 220 are shown in Table LXXI.

A fundamentally new proposal for the evaluation of negative film speeds was that made by Jones,[10] who considered the question of tone reproduction as applied to the final print and suggested a system in which the speeds assigned to the negative material are in terms of the exposure required to give a negative from which a print of specified quality can be made. Thus, instead of treating the negative obtained as the criterion of adequate exposure, Jones holds that the criterion is that the exposure must be such that prints of satisfactorily high quality can be made. Owing to the latitude of negative materials compared with the *brightness scale* of most scenes photographed, there is a large range of exposures through which there is little change in the quality of the prints, but the effective speed must be based on the *least* exposure which will give a negative from which a print of satisfactory quality can be made.

TABLE LXXI

DATA ILLUSTRATING THE RELATION BETWEEN THE VALUES OF SPEED BASED UPON INERTIA, i, AND THOSE BASED UPON THE EXPOSURE, E_m, CORRESPONDING TO THE MINIMUM USEFUL GRADIENT

T_d	γ	*Fog*	i	E_m	i/E_m
1.5	0.68	0.15	0.045	0.0280	1.6
2.0	0.80	0.22	0.025	0.0058	4.3
4.5	1.7	0.32	0.026	0.0053	4.9
6.0	2.0	0.47	0.024	0.0044	5.5
9.0	2.6	0.51	0.033	0.0050	6.6

The first question which arises is, what is a satisfactory print? Theoretically, this could be determined by the application of the theory of tone reproduction, dealt with in Chapter XX, by which the conditions might be found which would result in a print giving the same tone values as the original subject. However, if such prints could be obtained, it would not be right to assume that they would be chosen as the "best prints." Even if prints could be made which would reproduce the sensations arising when the observer looked at the original, it would not be justifiable to say that such a print was the "best print." In the choice of the best prints, much higher mental activities than the sensory ones are involved.

In the light of present knowledge, it seems best to judge the quality of prints by a statistical method. In that used by

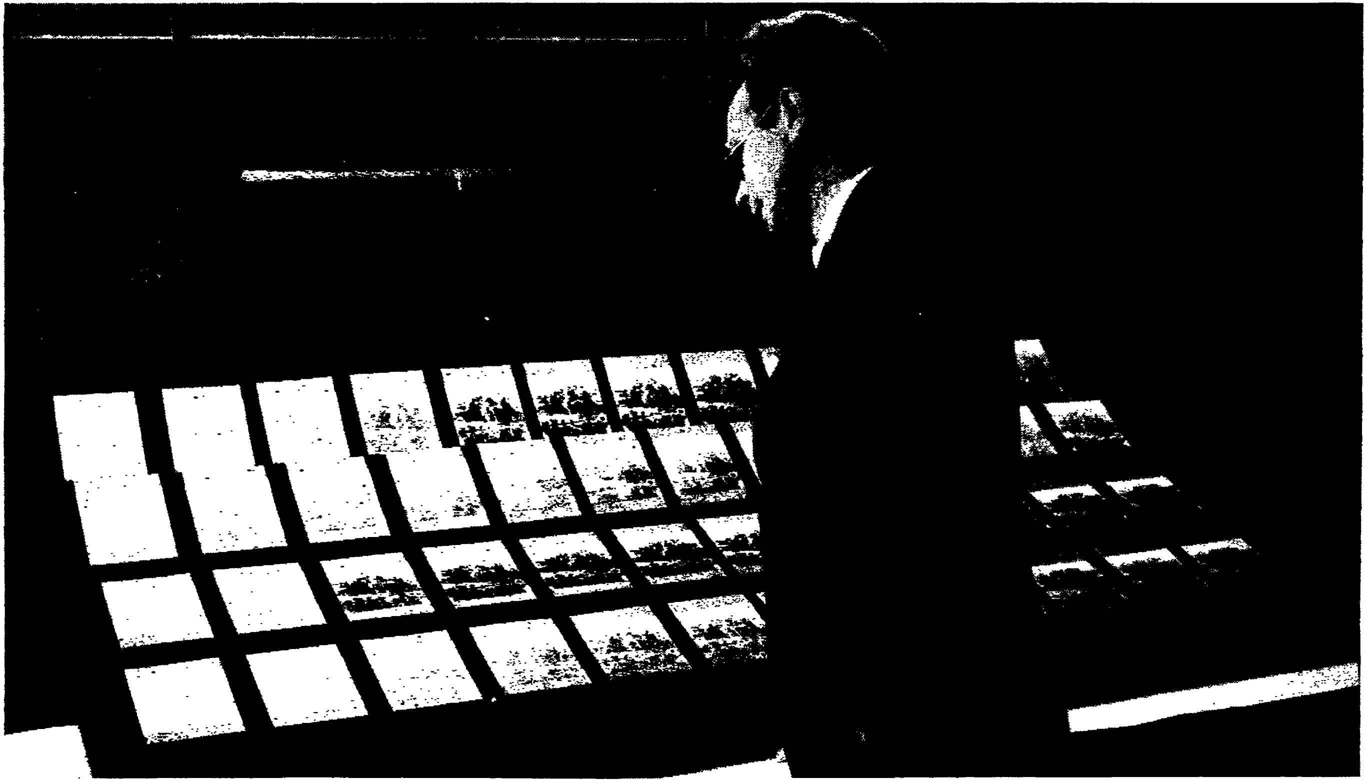

FIG. 221. Judging prints made from negatives given a series of exposures.

Jones, a series of twelve negatives in which the exposure was increased progressively from a very low to a very high value was made on each material to be studied. The scene chosen was an *average* one giving an image illumination range on the negative material of 32, which is very nearly the statistical average of a large number of scenes when photographed with a camera system having average flare characteristics. From each negative thus obtained, a skilled printer made the best possible print which could be obtained, using a paper chosen to fit the negative as regards contrast grade; and in order to cover the entire field, the printers were asked to use several grades of contrast and several printing exposures and then to pick a group of prints representing the best of those of which each negative was capable. These series of prints were then arranged in order and were judged by two hundred observers, each observer being requested to pick the first print in each series which he considered "excellent." This is, of course, a very laborious method

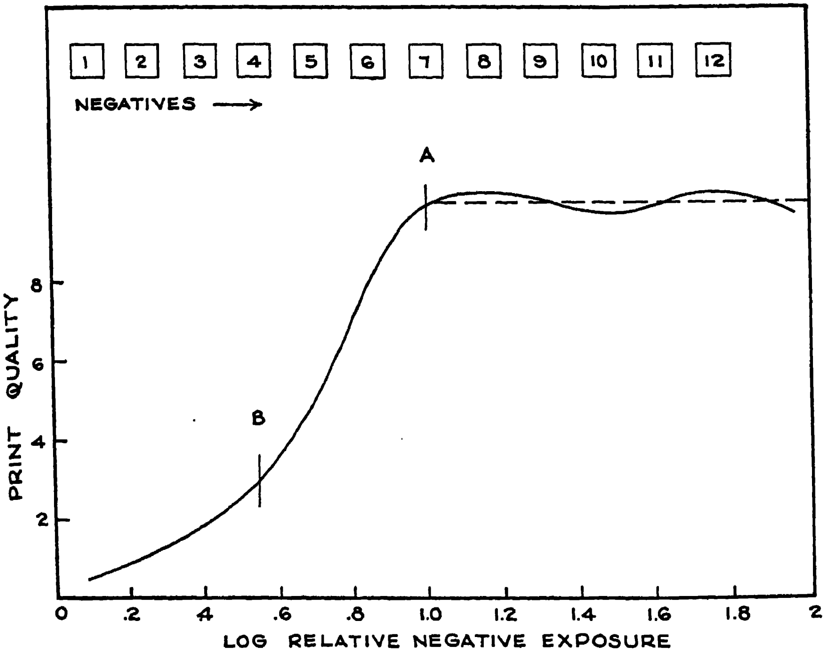

FIG. 222. Approximate relation between the quality of a print and the exposure of the negative.

of working, but it made it possible to obtain a statistical statement of the negative which the average observer would consider satisfactory (Figure 221). It was also possible for the observers to select a print inferior to the "first excellent" print, which might be called the *just acceptable* print. The judgment can be illustrated by the curve shown in Figure 222, which is not a quantitative, but a qualitative curve. It shows that the print quality as judged in the manner described by the agreement of a large number of observers improves as more exposure is given to the negatives until at the point B, corresponding to the fourth negative, the majority of the observers would agree that the prints were "just acceptable," while at the point A, corresponding to the seventh negative, they would agree that the prints were "excellent" and that further exposure for the negative produced no appreciable improvement in the quality of the print (Chapter XX, p. 818).

The camera speeds of the films tested could now be stated in terms of the least exposure necessary to give a negative which would give a print of "excellent" quality, as indicated at A, or of just acceptable quality, as indicated at B. In practice, it seems desirable to base speed on the exposure required to give a print of excellent quality, especially as the point A can be determined at least as sharply as the point B.

The statistical method of work is, of course, much too complicated and laborious to permit its application in practice, and for practical purposes it is imperative to find a sensitometric method which will yield results in close agreement with the direct statistical method. It was found that such a method could be used, and this is illustrated in Figure 223.

The curve A is the usual density-log exposure relationship for a negative material, and curve B is the derivative curve in which $\frac{dD}{d \log E}$ is plotted against $\log E$. The negative from which the first excellent print was obtained was found to use a portion of the characteristic A lying between the points M and O. Let the average slope of the used portion of the curve be designated by $\bar{G}$ and the slope at the point M by $G_{\min}$, this being the limiting gradient at the extreme shadow end of the object tonal scale. Then, the ratio of $G_{\min}$ to $\bar{G}$ is a measure of the relative contrast compression which occurs in the negative in the extreme shadow region, and this may for convenience be referred to as K, the shadow detail compression factor:

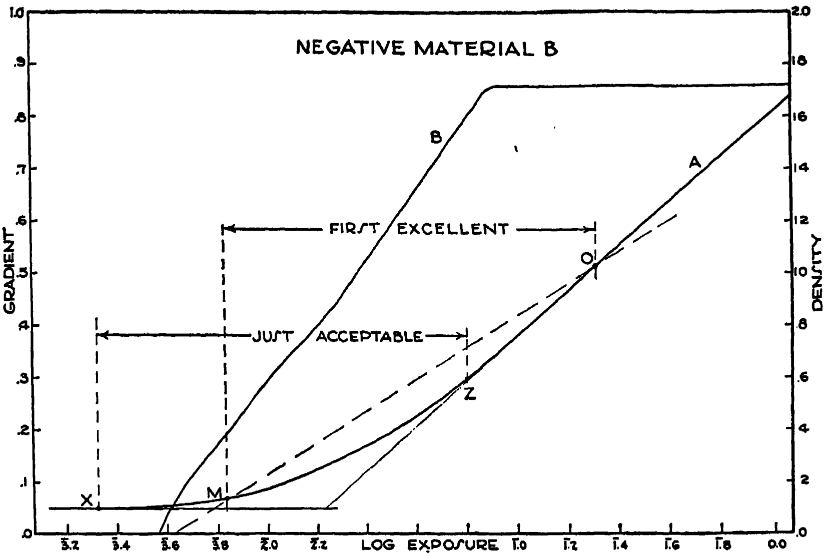

Fig. 223. Relation between the quality of prints and the characteristic curve of the negative.

$$K = G_{\min}/\bar{G}.$$

The values of K for four negative materials are shown in Table LXXII. It will be seen that the average of the four values is 0.30 and that the variation between the highest and the lowest value is relatively small. It should be emphasized that the exposure value corresponding to the point M is determined directly from the statistically chosen first "excellent"

TABLE LXXII

	$\bar{G}$	$G_{\min}$	$G_{\max}$	K	ΔK (%)
A	0.64	0.200	0.85	0.312	4.0
B	0.61	0.195	0.86	0.320	6.7
C	0.45	0.125	0.86	0.284	5.4
D	0.48	0.135	0.78	0.282	6.0
Mean				0.300	5.5

print and does not depend upon any sensitometric operation but is a direct result of an estimate of picture quality. If, now, it is assumed that the exposure value corresponding to the point *M* is a satisfactory criterion of the effective camera speeds of these four materials, speed values may be obtained from the reciprocal of these exposure values. These are shown in column *A* of Table LXXIII. If the speeds of these materials are determined in terms of the exposure corresponding to the point at which the gradient is 0.30 times the average gradient ($\bar{G}$) of the used portion of the characteristic curve, the values shown in column *B* are obtained. In the column $\Delta S(\%)$ are shown these same differences expressed as a percentage of the values in column *A*. It will be seen that the use of the average value of *K* for these four materials produces a negligible error in the speed value as based upon the print which, in the opinion of the two hundred observers used in this work, was considered to be the first excellent print.

TABLE LXXIII

	A	*B*	ΔS	ΔS (%)
A	166.0	169.8	3.8	2.3
B	144.0	150.8	6.8	4.1
C	118.0	112.7	5.3	4.5
D	89.0	84.4	4.6	4.5
Mean				3.9

This conclusion was checked by Jones and Nelson[11] in a study of the correlation between the speed values obtained from the first excellent print and the speed value as deduced from the exposure at which the gradient is 0.3 times the average gradient of the used portion of the characteristic curve. In this study, they used three different test objects, in which the contrast of the object varied from 12 to 100. They employed seventeen negative materials used commercially but differing quite widely with respect to speed and shape of the characteristic curve. Six different development formulas were employed, and in one case the development time was varied to give a fairly wide range in the extent of development. Most of the prints were made by contact on a paper which was available in six degrees of contrast, but six series were printed by projection. None of

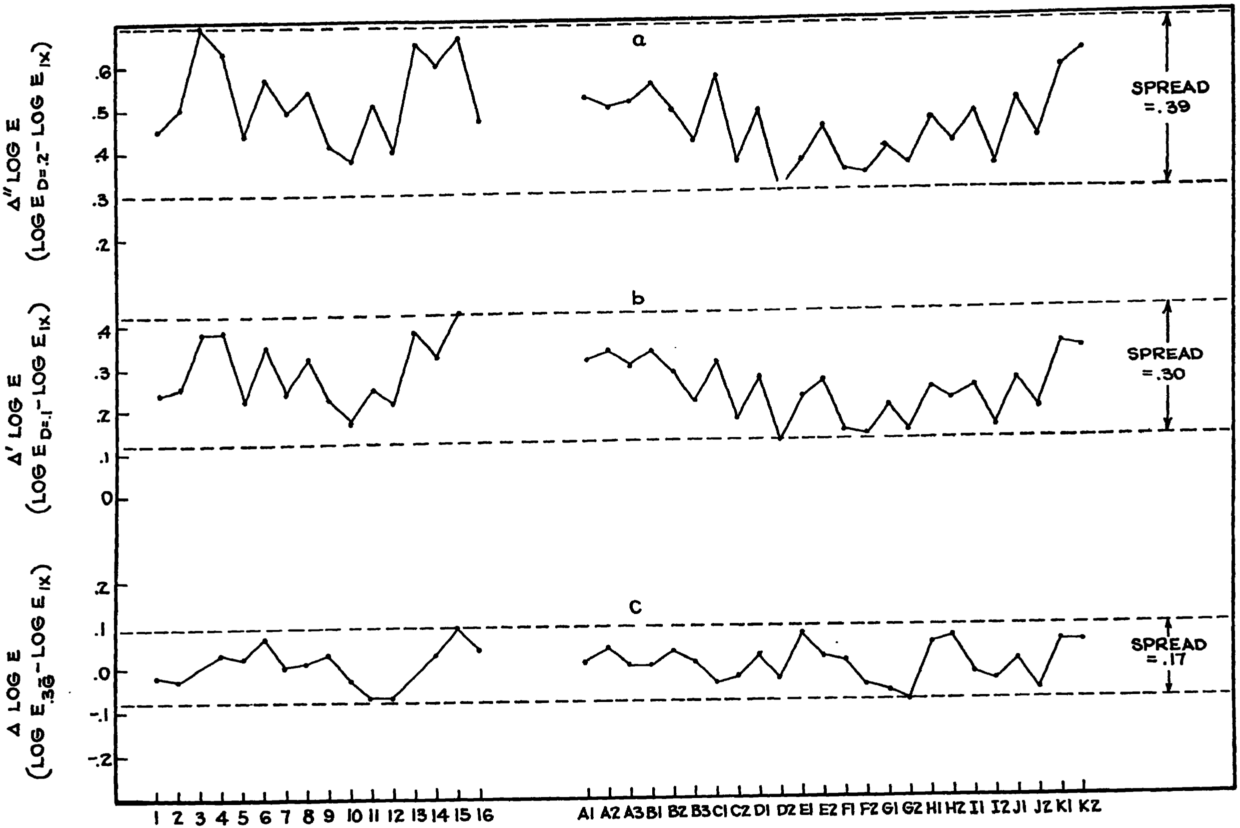

FIG. 224. Correlation between different methods of expressing speed.

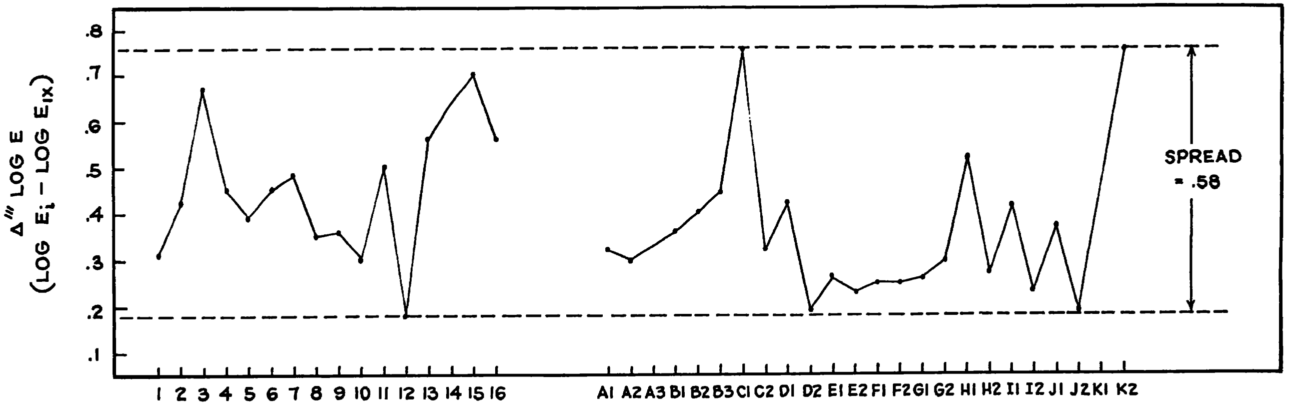

FIG. 225. Correlation between speed derived from the inertia point and from the negative giving the first excellent print.

these variables was found to affect in any systematic manner the observed value of K. It must be recognized, of course, that the value of K as determined from the statistical selection of the first excellent print necessarily shows a certain amount of variation; and if speed numbers are determined by using the average value of K, there will be certain discrepancies between the speed number obtained and that which would be obtained from the negative exposure resulting in the first excellent print. The relation between the two can be expressed by plotting the deviation between the speed numbers, based upon the different criteria.

In Figure 224, taken from Jones and Nelson's paper, are shown correlations between various methods of determining speed. These show for a large number of materials the deviation of the speeds obtained from the statistical determination of the first excellent print from the speed numbers obtained from some other criterion. In *a*, the second criterion is the log E value for which $D = 0.2$. In *b*, it is the log E value for which $D = 0.1$. In *c*, it is the log E value for which the gradient is 0.30 times the average gradient of that part of the D, log E characteristic covered by a range of log E values of 1.5. It will be seen that the spread of log E values between the two methods of determining speed is only 0.17 in curve *c*, as compared with 0.30 in curve *b* and 0.39 in curve *a*.

The superiority of this method of determining speed to the use of the inertia is seen by comparing Figure 224 with Figure 225, in which the spread is plotted between speeds derived from the selection of the negative giving the first excellent print and the logarithm of the inertia point. The spread here is 0.58, more than three times the spread attained when the fractional gradient is used as the criterion.

The cause for the inferior results obtained with the criteria based on fixed densities and on the inertia will be seen by considering Figures 226 and 227. The photographic material illustrated in Figure 226 has a long sweeping toe, so that the portion of the characteristic A–B used in making the first excellent print has a relatively low average gradient. The shape of this part of the curve is such that it approaches fairly closely to the mirror image of the D, log E characteristic for the No. 4 contrast grade of the developing-out paper used for making the positives, and

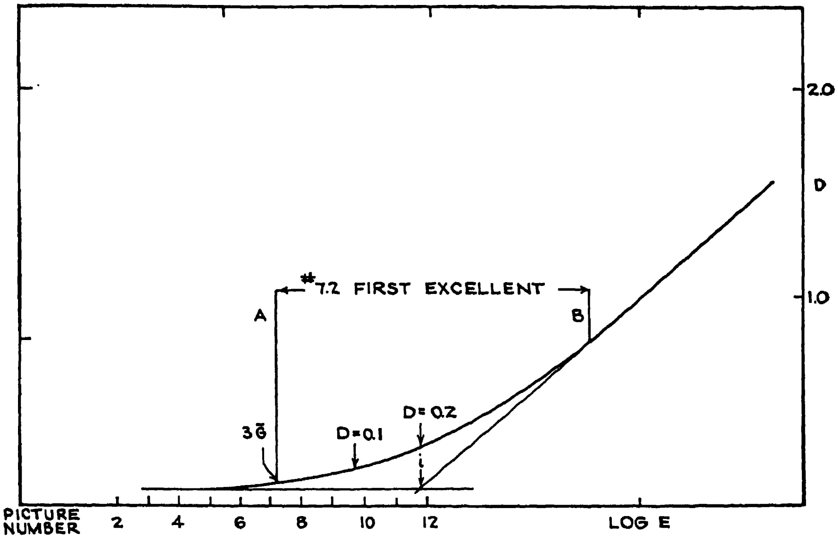

Fig. 226. Characteristic curve showing long sweeping toe.

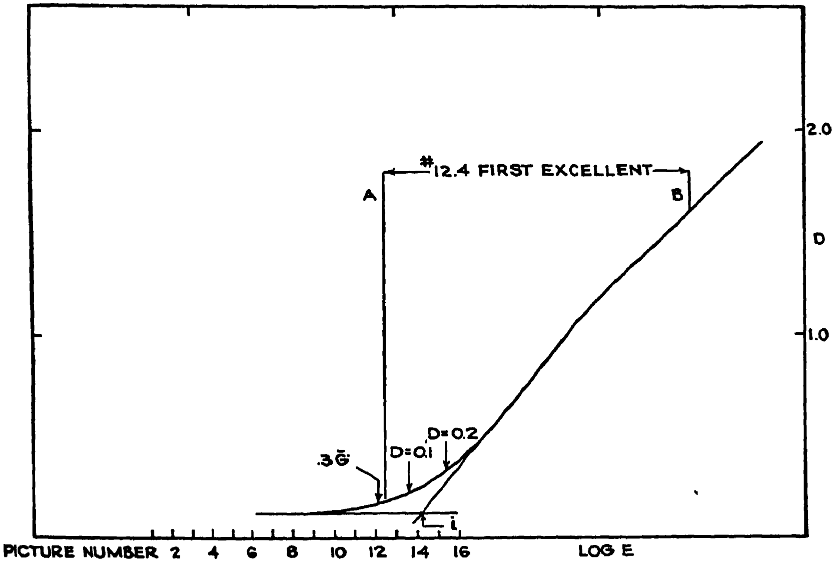

Fig. 227. Characteristic curve showing sharp toe.

the large group of observers who judged the quality of this group of prints agreed substantially that this print was the "first excellent" print in the series. There can be little doubt that this print actually does have excellent photographic quality, being practically as good as any of the prints made from negatives which have received more exposure. Because of the relatively low gradient in the lower exposure parts of this curve, a rather great increase in exposure is required to reach the points where $D = 0.1 + \text{fog}$, $D = 0.2 + \text{fog}$, and the inertia point.

On the other hand, the material illustrated in Figure 227 has a rather sharp toe rising quickly into a straight-line region of relatively high gradient. The average gradient of the portion of the curve used for making the first excellent print is relatively high, being 0.94 compared with 0.45 in the case of material shown in Figure 226. The contrast grade of the developing-out paper which gave the best fit with material shown in Figure 227 was No. 1, and here again the group of observers making the judgment agreed that this combination of paper and negative resulted in the "first excellent" print. Since the gradient increases rapidly with increasing exposure, only small exposure increments are required to reach the points where $D = 0.1 + \text{fog}$, $D = 0.2 + \text{fog}$, and the inertia point. The points corresponding to $0.3\ \bar{G}$, however, fall very close to the extreme shadow densities of the negative in both cases. It is apparent, therefore, that with materials differing from each other with respect to curve shape, as illustrated by the materials in Figures 226 and 227, the fixed density and inertia criteria cannot be expected to agree as well with the "first excellent" print speeds as speed numbers based upon the fractional gradient criterion.

Jones and Nelson extended their work to cover a great range of negative materials, making a study of some seventy-eight additional materials and determining the correlation between the speed numbers based on various sensitometric criteria and those derived from the fractional gradient criterion; that is, from the $\log E$ value corresponding to a gradient of 0.3 times the average gradient. The correlation already shown between the fractional gradient speeds and the print judgment speeds was so good that they felt justified in assuming that the fractional gradient speeds of the additional group of materials would agree closely with the print judgment speeds. The most important of the other speed criteria was that corresponding to the German DIN specification, in which the criterion is the exposure required to produce a density equal to 0.1 above fog, the development being carried to such an extent that the maximum possible speed number is obtained. The deviation between the fractional gradient value and the DIN speeds obtained in this way was very high, the total spread in log E units being 0.9, so that it would be possible to select from this group two materials having the same fractional gradient speed, one of which would be eight times as fast as the other when determined according to the DIN specification.

If, instead of using the optimal development, normal development was employed, that being defined as the development which would give an average γ for the seventy-eight materials of 0.9, the spread between the extreme rates of speeds by the two methods is reduced to 0.43; and the range of speeds obtained, therefore, would be only a little over 1 : 2 instead of 1 : 8.

The use of the Hurter and Driffield method under these conditions gave a spread of 0.63 and a speed ratio of slightly over 1 : 4. It is, however, worth noting from the figures given by Jones and Nelson that the inertia gives very fair correlation with the fractional gradient speed on most of the materials. The elimination of six materials would make the log E spread of the order of 0.2. The fact is that the H and D inertia is nearly parallel to the gradient speed for *most* negative materials, but there are certain materials in wide use for which the speed as determined by the inertia is very different from that obtained by the fractional gradient criterion or by the direct experimental determination of the exposure required to give the "first excellent" print.

The determination of the effective speed of a material by the fractional gradient method involves the determination of two gradient values. Tuttle[12] describes instruments with which these measurements can easily be made. One of these instruments takes the form of a transparent sheet of material which is superimposed on the characteristic curve. As shown in Figure 228, the sheet carries two parallel lines, CD and EF, separated by a distance equivalent to a log E value of 1.5 on the curve to be analyzed. At the point *A*, there is pivoted another sheet on which is engraved the straight line *AB* and the curve *GH*, the point *G* being spaced 1.9 log *E* units from the center of the pivot. The shape and position of the curve *GH* are determined by the position of the pivot point and the requirement that the minimum gradient, which is the slope of the line *AB*, must be equal to 0.3 times the average gradient. In use, the meter is placed on the graph with the lines *CD* and *EF* parallel to the density axis (Figure 228). It is set with respect to the graph to a position where the lines *EF*, *GH*, and the characteristic curve intersect at a common point while simultaneously the lines *AB* and *CD* intersect at another point on the toe of the curve. The meter parts are kept in an orientation such that these lines always intersect while the device as a whole is slid along the characteristic curve. At some point, the line *AB* becomes tangent to the characteristic curve, at which point the gradient is equal to 0.3 times the average gradient over the

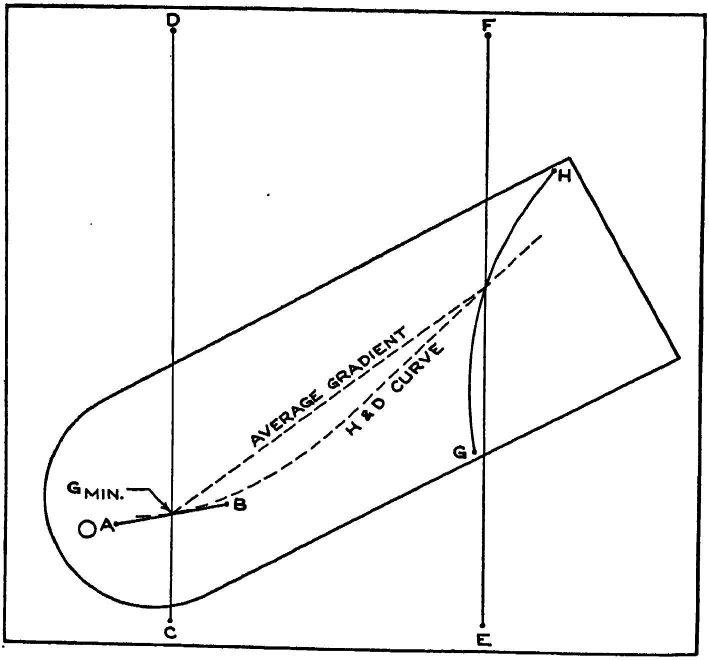

FIG. 228. Transparent meter for determining gradient speeds from the characteristic curve.

1.5 log *E* interval. The point of tangency can usually be located after two or three trials, and the speed of the emulsion is determined by the abscissa value of this point.

There is much to be said for a method of speed determination which avoids entirely the determination of the characteristic curve. If, instead of the usual step-by-step sensitometric strip, a continuous wedged exposure is impressed on the material to be tested, the gradient may be read directly. Any comparison beam densitometer may be used to make a direct reading of the gradient of a wedged strip if the beams can be directed through areas on the wedge which are separated by a known log *E* increment. The gradient ratios can be determined directly if the wedge strip is divided into three sections, as shown in Figure 229, exposed so that at all points the second wedge *B* receives a slightly greater exposure than *A*, while the third, *C*, receives 1.5 log exposure units more than *B*. The limiting gradient value may then be determined from the density difference between corresponding points on the first and second wedges divided by the log *E* increment by which the exposures are separated. The average gradient can be determined by a similar comparison of the second and third wedges. A simple photometric device can be made for analyzing such strips.

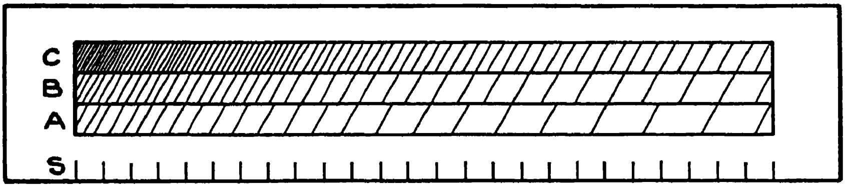

FIG. 229. Triple sensitometric wedged exposure.

Elaborating this system, Tuttle designed a direct photoelectric method for measuring gradients and applied it to an instrument employing a double optical wedge, by which the emulsion speed can be read automatically.

As the instruments described above are rather specialized tools, Tuttle[13] suggested a mathematical method of analyzing conventional sensitometric data. The gradient-speed value is derived from the exposure point at which the gradient of the characteristic curve is 0.3 × the average gradient over a range of 1.5 in logarithmic exposure units. In practice, instead of the limiting gradient being $\frac{dD}{d \log E}$, it can be written $\frac{D_2 - D_1}{0.3}$, where D_1 and D_2 are densities on the toe of the curve produced by exposures one of which is double the other. The average gradient is $\frac{D_3 - \frac{1}{2}(D_1 + D_2)}{1.5}$, where D_3 is the density produced by an exposure of which the logarithm is 1.5 greater than that corresponding to a density which lies on the curve at the mid-point between D_1 and D_2 and which, therefore, is equal to approximately $\frac{1}{2}(D_1 + D_2)$. Thus, when the limiting gradient is 0.3 times the average gradient,

$$\frac{D_2 - D_1}{0.3} = 0.3 \frac{\left(D_3 - \frac{D_1 + D_2}{2}\right)}{1.5},$$

which may be simplified and approximated to

$$17D_2 - 16D_1 = D_3.$$

By using a table of the density values read from a sensitometric strip having exposure intervals of $\sqrt{2}$, the values of D_1 and D_2 may be written and the value of $17D_2 - 16D_1$ may be calculated. When $17D_2 - 16D_1 = D_3$ in the table, the log E value corresponding to $\frac{D_1 + D_2}{2}$ may be determined by interpolation.

THE DEVELOPMENT CONSTANTS

The constants which define the rate of development of a photographic material are k, the velocity constant, and γ_∞, the maximum γ available when the development is prolonged. The value of k depends not only upon the material but also upon the developing solution and the temperature. In Figure 230 are shown the γ, t curves for the same material in two different developing solutions, the value of γ_∞ available on extended development being the same. In the case of curve A, the γ increases at a much greater rate than in the case of curve B; that is, the velocity constant of development, k, is much higher, but if the development time is sufficiently lengthened in the case of curve B, the same maximum γ will be attained. The relation between the value of γ and the time of development is expressed by an exponential equation (Chapter XI, p. 409) of which the simplest form is

$$\gamma = \gamma_\infty(1 - e^{-kt}).$$

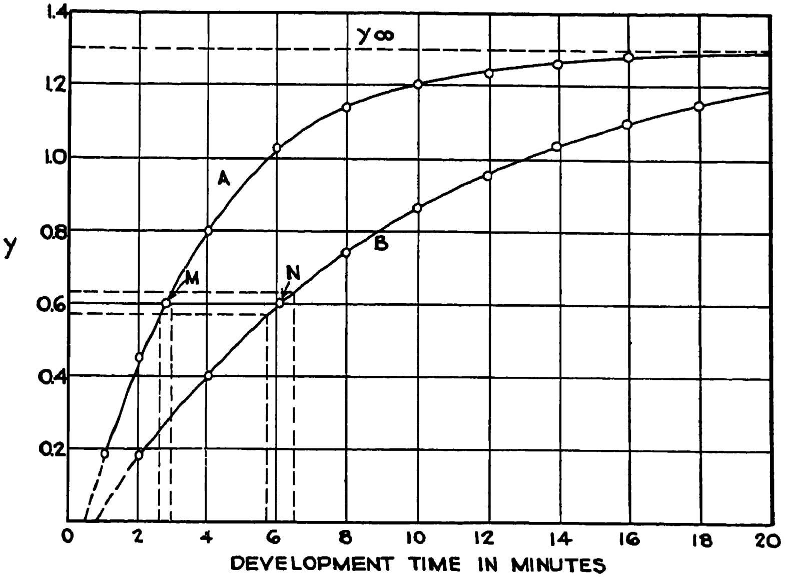

FIG. 230. γ, *t* curves of the same material in two developing solutions.

L. N. G. Filon suggested to Sheppard and Mees[14] that if two sensitometric strips were developed, one for twice the time of the other, so that $t_2 = 2t_1$, the simultaneous equations

$$\gamma_1 = \gamma_\infty(1 - e^{-kt_1}),$$
$$\gamma_2 = \gamma_\infty(1 - e^{-kt_2})$$

would be obtained. These equations give

$$\gamma_1(1 - e^{-kt_2}) = \gamma_2(1 - e^{-kt_1}),$$

and since

$$t_2 = 2t_1,$$

$$\frac{\gamma_2}{\gamma_1} = (1 + e^{-kt_1})$$

or

$$\frac{\gamma_2 - \gamma_1}{\gamma_1} = e^{-kt_1},$$

$$k = \frac{1}{t_1} \ln \frac{\gamma_1}{\gamma_2 - \gamma_1}.$$

k having been found, e^{-kt_1} can be found, and

$$\gamma_\infty = \frac{\gamma_1}{1 - e^{-kt_1}} = \frac{\gamma_2}{1 - e^{-kt_2}}.$$

The calculation of k and γ_∞ is greatly facilitated by tables giving the relation between k and $\frac{\gamma_2}{\gamma_1}$ and between kt and $1 - e^{-kt}$. A simple graphic method by which γ_∞ and k can be read from charts constructed from these tables is given by Renwick.[15] Heydecker[16] also gives a very simple graphic method for the evaluation of γ_∞ from measurements of γ_1 and γ_2 and methods for the calculation of k and of the time of development required to obtain any given value of γ.

In practice, the theoretical relationships given above do not hold in all cases since development does not always proceed according to the simple equations given, the validity of these relationships depending upon the normality of the family of D, log E characteristic curves. It is therefore often convenient to determine γ_∞ experimentally, plotting the γ, t curve obtained by developing sensitometric strips for various times and deducing the value of γ_∞ as the limit to which γ approaches; k can then be found from the differential equation

$$\frac{d\gamma}{dt} = k(\gamma_\infty - \gamma),$$

since $\frac{d\gamma}{dt}$ is the slope of the γ, t curve. The values of k computed in this way for various values of γ should, of course, be the same, and in practice when such a γ, t curve is derived from the normal family of characteristic curves and the experimental determination of γ_∞ is valid, k will be found to be constant.

Certain development characteristics of any particular photographic material may be deduced from the values of γ and k:

If k is high and γ_∞ is high, development starts quickly, proceeds at a high rate, and γ continues to build up to a high value. Process films and motion-picture positive film are typical examples of materials having these characteristics.

If k is high and γ_∞ is low, the image flashes up quickly; and γ builds up rapidly at first but soon ceases to increase, reaching a limit at a relatively low value. In the case of these materials, the image appears very quickly but fails to carry through and build up high densities.

If k is low and γ_∞ is high, development starts slowly, and γ increases at a relatively low rate; but by an extension of the time of development, the value of γ may be built up to a high value.

If k is low and γ_∞ is low, development starts slowly, γ increasing at a relatively low rate, which very soon decreases and flattens out at a final low value. Further development does not increase contrast.

The γ, t curve is of use where it is desired to determine the development time which will yield some specified value of γ. If such a curve is available for the material and the processing conditions being used, it is only necessary to read from the curve for any γ value the corresponding development time. Such curves are also very useful in obtaining some idea as to the permissible variation in development time when it is desired to control processing so as to obtain γ values lying within certain prescribed limits. For instance, let it be assumed that it is desirable to obtain a γ of 0.6 and that the permissible variations from the value are set at ± 0.03. The corresponding permissible variation in development time can be readily determined for the two conditions represented by curves A and B (Figure 230). The horizontal dotted lines are drawn through γ values of $0.60 + 0.03$ and $0.60 - 0.03$. Where these horizontal lines intersect with curves A and B, perpendiculars are dropped onto the development time, T_d, axis. In the case of curve A, it is found that the development time must be held between 2.6 and 3.0 minutes, thus permitting a total allowable variation of 0.4 minute, which may be expressed as 2.8 ± 0.2 minutes. In the case of curve B, it is found for the same tolerance in γ, minimum time of 5.7 and the maximum 6.5, which may be expressed as 6.1 ± 0.4 minutes. It is evident, therefore, that the allowable error in development time for the required precision in control of γ is twice as great in the case of curve B as for curve A. The relation between a given γ increment and the corresponding development-time increment is, of course, given directly by the gradient of the γ, t curve at any particular point. If it is desired, therefore, to express numerically this relationship, it is only necessary to evaluate the differential $\frac{d\gamma}{dt}$ at any given point. The value of the differential at any point is inversely proportional to what may be termed *processing latitude.* In other words, the greater the gradient of the γ, t curve at any point, the more precise must be the control of processing conditions in order to maintain a given tolerance in γ.

THE SENSITOMETRIC CONSTANTS OF PRINTING PAPERS

The sensitometric properties of photographic papers can be described by means of a series of numerical constants parallel to those used in the sensitometry of negative materials. These were originally defined in the paper by Jones, Nutting, and Mees,[17] in which they published their study of the sensitometry of photographic papers.

The first constant of importance for the standardization of a paper is the *maximum black;* that is, the reflecting power of the heaviest deposit that can be obtained on the paper with full exposure and development. Such a deposit may reflect from 1 per cent to 10 per cent of the incident light; deposits reflecting above 8 per cent give visibly grayish blacks, those from 6 per cent to 3 per cent are strong blacks, and any deposit reflecting less than 3 per cent appears a very intense black.

The reflecting power of a paper is expressed not as a percentage but as the logarithm of the reciprocal of the reflecting power, so that paper having a reflecting power of 5 per cent would be read as a density of 1.3. Most papers give maximum densities between 1.3 and 1.6, a few papers being under 1.3, while occasional papers give values as high as 2.0. Other things being equal, a glossy paper gives a higher maximum black than the same paper with a matte surface, because the matte surface always involves light scattered from the gelatin or from materials in the emulsion other than silver. Thus, a glossy paper of a certain type gives 1.63 as its maximum black; a semimatte paper, 1.50; and matte paper, 1.28, the intensity of the black decreasing as the surface becomes more matte. At the same time, the maximum black is an important characteristic of the emulsion, apart from its contrast or surface, and a high reading of maximum black is an indication of good quality in the paper. To sum up, matte papers should give readings of maximum black from 1.10, as a minimum, to 1.40; semimatte papers, from 1.35 to 1.60; and glossy papers, from 1.50 to 1.80.

The *contrast* of a printing paper is a very complex matter; it involves psychological as well as purely physical considerations. In addition to the value of maximum black, two sensitometric constants are directly related to the contrast of a paper. The first of these is a specification of the slope or gradient characteristics of the curve. In the earlier work on the subject, this was defined as the slope of the straight-line portion corresponding to the γ of the characteristic curve of a negative material. More recently, it has been found that the straight-line portion of paper curves covers such a small range of exposures that it has little significance in relation to the performance of the material. A more valuable characteristic than the slope of the straight-line portion is the *maximum* slope of the curve ($G_{\max}$), which in many cases is the slope at the inflection point of the curve. In the case of photographic papers, the velocity of development is high, and hence the slope reaches its maximum very quickly. In practice, therefore, the slope is almost always of the maximum value that it is possible to obtain with the paper used.

The second factor affecting contrast is the *total scale* of a paper. Total scale may be defined as that range of light intensities, expressed in exposure or log exposure units, which can be reproduced by the paper as areas differing perceptibly in density. The method of fixing the scale limits is best explained by reference to Figure 231. The curve A is the characteristic curve of a paper plotted with log E as abscissa and density as ordinate. Curve B is the first derivative of A, the value of the ordinate at any point on B being the slope of curve A at the corresponding point. The total scale of the paper is the distance (measured on the log E axis) between certain points on the curve at which the slope is so small that the change of density with exposure may be considered to be negligible. The smallest perceptible difference in the density of two areas is about 0.02; hence, at the point where the slope is 0.2, a difference of about 25 per cent in exposure is required to produce a perceptible difference in the density of the resulting deposit. The points at which the slope is 0.2 therefore provisionally represent the limits of the exposure scale. On curve A, the points x and y mark the limits of total scale, in this case the value of total scale being 1.75 (2.25 − 0.50) in log exposure units, or 56.2 in exposure units. To the left of x and to the right of y, exposures differing by more than 25 per cent are required to produce a perceptible difference in density and hence are not considered useful parts of the scale. As will be shown later, the true value of the limiting gradient is not constant but increases with the contrast of the paper. Papers of high contrast have a shorter effective exposure scale than is indicated between the points where the gradient is 0.2.

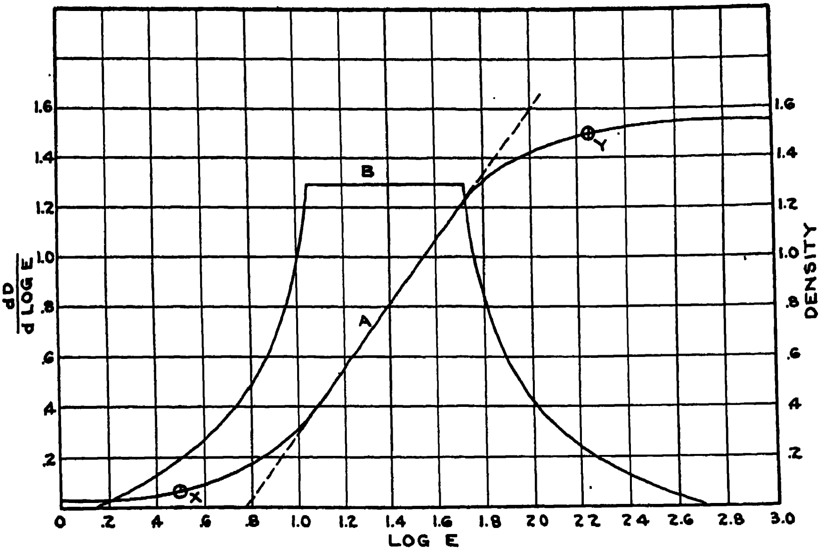

FIG. 231. Characteristic and derivative curves for a paper material.

It is quite possible for two papers to have the same scale but different slope characteristics. This is shown in Figure 232, where the paper marked B has a much steeper slope than the one marked A, though both have the same total scale value; namely, 1.60.

When a paper is chosen for printing a given negative, it is obvious that, if all different gradations on the negative are to be rendered as different gradations in the print, the scale of the paper must be at least as great as the difference between the maximum and minimum densities of the negative. Even when this condition is fulfilled, some detail may be lost in the extreme shadows and highlights; hence, the condition is necessary but not sufficient. If the maximum density of a negative is 1.7 and the minimum density 0.3, the difference being 1.4, the printing paper to render this negative must have a total scale of at least 1.4 in log exposure units.

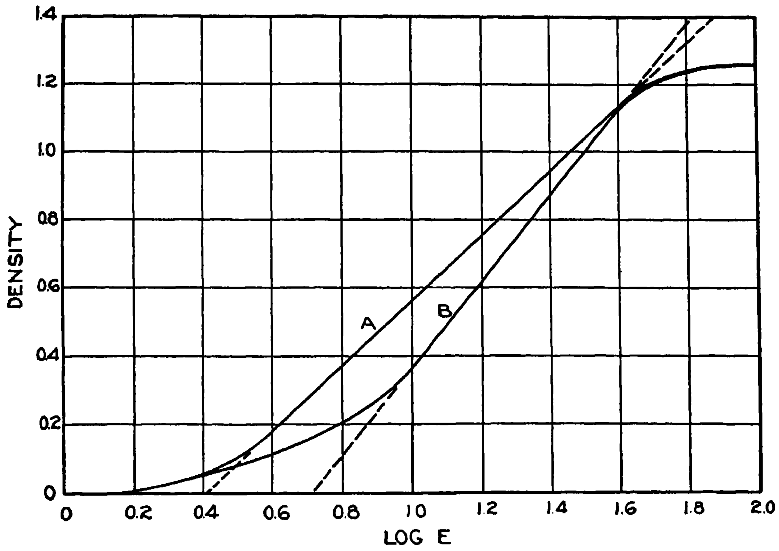

FIG. 232. Characteristics of two papers having the same scale but different slopes.

Papers differ greatly in their total scale. The hardest printing papers used for amateur work have a log scale as low as 0.7; the ordinary papers chiefly used, 1.0; and the softer papers, from 1.2 to 1.5. For portrait work, papers with a log exposure scale of 1.5 are commonly used. Papers for enlarging have scales varying from 0.8 to 1.5. The gradient values of the papers also vary considerably, the harder papers giving the greater values.

In practical photographic printing, a printing paper for a given negative is selected by the rule that the density scale of the negative is equal to the *effective exposure scale* of the paper. In order to determine the contrast of a printing paper, the effective paper exposure scale must be defined; also, it is necessary to know whether this effective scale is independent of the negative.

Jones[9] made a statistical study of the problem as follows: A large number of printing papers was selected; and, on these, prints were made from negatives of different γ's, the subject being a landscape having a photographic brightness scale in the camera of 1 : 27. In order to allow for individual preference, three printing times were given each negative. One print was that which a printer would consider normal; one, slightly lighter; and one, slightly darker. In this way, nine prints, representing generally three prints from each of three negatives of different γ values, were made and mounted on panels. The prints were then judged by seventy-five observers, divided into groups according to their knowledge of photography. Each individual selected from each panel the print that he considered best. From the negative selected for each paper, it was possible to determine the γ of negative which, in the opinion of the average observer, gave the best results on that paper. It was found that the value of γ for the best negative was not a measure of the contrast of the paper. In many cases, papers of obviously *different contrasts* gave their best prints from negatives of the *same* γ. This led to a study of the factors which determine the contrast of papers. It may be said in passing that the different groups of observers showed no wide divergence according to their knowledge of photography and that, on the whole, they agreed very closely in their judgment.

Before Jones' work on the contrast of papers is discussed, reference should be made to the work of Bontenbal,[18] who compared the various criteria which have been proposed for the statement of contrast using a statistical method analogous to that used by Jones. He found five of the formulas, including that of Jones, in close agreement with his statistical data. Three of them, however, are the average gradients or exposure scales in a range the upper limit of which is given by $D_{\text{max.}} - 0.1$. If these criteria were generally accepted, it would be very easy to produce papers of high contrast by providing for a very low value of $D_{\text{max.}}$. The fourth criterion, that proposed by Reinders and Bontenbal, is the exposure scale between $D = 0.25$ and $D = 0.9$. The judgment of contrast should not, however, ignore the highlights and deep shadows. The agreement of this criterion with the results obtained by Bontenbal was probably due to the fact that the papers which he used had rather well-balanced characteristic curves.

It has been said that, in defining the exposure scale of a paper, it has been accepted provisionally that the limiting gradient has a value of 0.2; that is, the curve is assumed to terminate at the point where the gradient is 0.2, at both the top and bottom of the curve, and the exposure range is read between these two points.

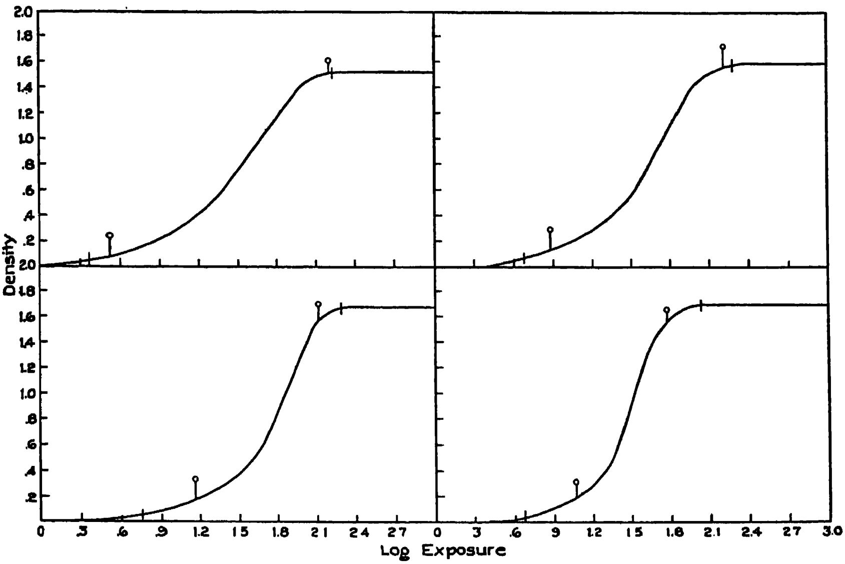

FIG. 233. Characteristics of four grades of paper showing their scales.

From the result of his statistical inquiry, Jones found that, when the negative was flat, and, therefore, the paper used was contrasty, greater limiting gradient was required than when the paper was flat. Papers of high contrast therefore have a shorter effective exposure scale than that indicated as lying between the points where the density gradients have a numerical value of 0.2. Thus, in Figure 233 are shown the curves of four different grades of printing paper. On each curve, the points where the gradient is 0.2 are indicated by plain vertical lines; and those where the scale actually stopped, by lines carrying a circle. In No. 1, the scale selected by judgment was from the point where the gradient was 0.27 to the point where it became 0.30.

In No. 2, the minimum value at the bottom of the curve was 0.36 and at the top, 0.34. In No. 3, the values were 0.49 and 1.00 and in No. 4, 0.64 and 1.02. Upon further analysis of the figures, it became clear that this might have been expected, the true law being that the limiting density difference of the print compared with the object is constant; that is, the eye requires a certain minimum contrast in the reproduction of the shadows. The limiting gradient of the paper depends upon the γ of the negative from which it is printed; the limiting gradient multiplied by the γ being equal to a value which is approximately a constant; so that, instead of the effective exposure scale of the printing paper being constant, it is actually dependent, to some degree, upon the γ of the negative. Further, the product obtained by multiplying the limiting gradient by the γ of the negative is not quite constant but, to some extent, depends upon the density scale of the print.

Goldberg[8] studied the limiting gradient of prints in shadows and highlights and came to the conclusion that the gradient in the shadows is much greater than that in the highlights. The results quoted above do not fully confirm this but are confined to the study of a single scene. If a number of different scenes are considered, it will be found that Goldberg's conclusion is correct and that the gradient in the shadows is generally greater than that in the highlights.

The effective, useful exposure scale of any given paper is therefore dependent upon the contrast of the subject. A subject of high contrast requires a negative of low γ when it is to be printed on a contrasty paper, in order that the density scale of the negative shall not exceed the exposure scale of the positive material. Since the γ of the negative is low, the limiting gradients of the characteristic curve of the paper must be high; and, hence, the effective exposure scale must be appreciably less than the total exposure scale. Conversely, for a subject of low contrast, the negative must be developed to a high γ in order to make its density scale approximate the exposure scale of the positive material. Since the γ of the negative is high, the limiting gradients of the paper curve may be low, and thus a much greater proportion of the total available exposure scale can be utilized. Flat subjects therefore enable the photographer to use a greater proportion of the exposure scale of a given paper than more contrasty subjects.

In addition to the fact that the effective exposure scale and, thus, the *effective contrast* of a paper is dependent upon the γ of the negative and, consequently, upon the objective contrast (brightness scale) of the subject, Jones[9] was able to formulate a general expression by which the contrast of a paper can be defined in terms of its characteristic curve. The evaluation of contrast proposed by him is based essentially upon the Weber-Fechner law, which states that

> "In order that differences of sensory experience, sensation, shall have in two different cases of comparison the same value for our reacting consciousness or shall appear to be equal, the stimuli that are compared in the two cases must differ from one another, not by the same absolute physical difference in their magnitude, but by the same relative difference."

While this law does not hold over the entire range of visual response, it has been shown to be valid for the brightness values commonly encountered in viewing photographic prints (p. 813). It follows, in the case of a two-part visual field, the brightness values of which are represented by 1 and 2, that if a definite *brilliance* (sensation) difference is produced, then in another two-part visual field the same *brilliance* difference will be produced by brightness values of 2 and 4, or of 4 and 8, or of 8 and 16, etc. Therefore, within the range for which the law is valid, it may be said that the sensation is directly proportional to the logarithm of the brightness. In such a simple field, the magnitude of subjective contrast (brilliance contrast) may be defined as directly proportional to the logarithm of the ratio of the brightness values. Brilliance contrast (subjective) $= \log B_1/B_2 = \log B_1 - \log B_2$.

In a complex grouping of brightness values, such as exists in a photographic print, there is a factor (other than the ratio of maximum to minimum brightness) which has a marked influence on the contrast impression. For instance, consider two objects in which the limiting brightnesses are identical and, therefore, of identical brilliance contrast when this factor is evaluated solely from the logarithm of the ratio of the maximum to minimum brightness. In one case, the transition from the low to high value of brightness may occur in a few steps of relatively great magnitude, while in the other the transition may occur by a large number of small brightness differences. Under such conditions, a greater *contrast* exists in that object where the transition from low to high brightness is rapid. In evaluating contrast, therefore, it is necessary to consider not only the absolute magnitude of the brightness interval but the rate of transition from one brightness to the other. The magnitude of the contrast sensation may thus be said to be a function of two independent variables, one of which may be referred to as the *rate* or *gradient* factor of contrast and the other as the *extent* or *altitude* factor.

The visual impression of contrast may be compared to the *muscular effort* involved in climbing a hill. This effort is proportional to the *altitude* and to the *slope,* or the *rate* at which the weight of the body must be lifted. While the work involved in this operation is a function only of the mass and the height through which it is lifted, the muscular effort involved depends very much on the rate at which the work must be done.

In the application of these general principles relating to contrast to the particular case of photographic prints, it is assumed that the print in question is viewed under uniform illumination. The various brightness values may be expressed in terms of density. Brightness is directly proportional to the reflection factors of the various areas of the print, and, since density is a logarithmic function of the *reciprocal of* reflecting power, it follows that density is a logarithmic function of the *reciprocal of* brightness. In order to express the brilliance contrast existing between *two* areas of a print, it is only necessary to specify the density difference, $D_2 - D_1$, which is equivalent to the term $\log B_1 - \log B_2$ used in specifying contrast in terms of brightness. Figure 234 shows the characteristic curves of three materials of different types; in the case of curve B, a given difference in exposure, $\Delta \log E$, is reproduced by the material whose characteristic is specified by this curve as a density difference ΔD_2; with another material, curve A, the exposure difference is reproduced as a density difference ΔD_1. If the reproduction of an object consisting of only two brightnesses were being considered, the magnitudes of ΔD_1 and ΔD_2 would be an adequate specification of the contrast of these materials. This is not the case, however, for the evaluation must be extended to include a large number of brightness values. The same exposure difference, $\Delta \log E$, rendered at another point on the curve for material *B*, for instance, at *mn*, produces a density difference, ΔD_3, which is obviously less than ΔD_2.

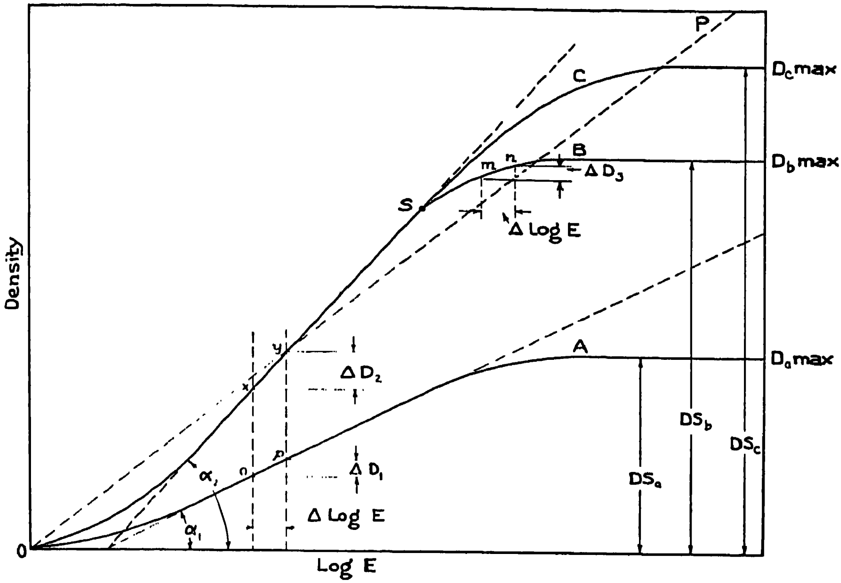

FIG. 234. Characteristic curves of three printing papers having different contrasts.

The rate of change of density with respect to exposure, while it does not constitute a complete specification of contrast, is an important factor in its determination. However, since *contrast* is usually used with reference to the characteristics of a material when its entire density scale, or a relatively large portion thereof, is utilized, some other factor must be considered. This is forcibly illustrated by the following example: Referring again to Figure 234, the curve designated as *C*, representing a third photographic material, has the same mean value of $dD/d \log E$ as curve *B*; in fact, the two curves are coincident up to the point *s*. Judged solely by the value of the differential $dD/d \log E$, these two materials are practically identical in contrast. Material *C*, however, has a higher value of maximum black and, hence, the density scale is greater than in the case of material B. It is possible on material C, therefore, to produce prints in which the value of $(D_{max} - D_{min})$ is appreciably greater than on material B. There is little doubt that such a print made on material C would be classified as more contrasty than one made on material B. *Contrast* as applied to photographic materials is therefore dependent upon two factors, which may be designated in general terms as rate and extent, the former of these being dependent upon the differential of density with respect to log exposure, while the latter is dependent upon the density scale.

The method of evaluating quantitatively the extent factor of contrast is fairly obvious. It is only necessary to determine the difference between the maximum and minimum densities for that portion of the characteristic curve to which the evaluation is to apply.

In evaluating the rate factor of contrast, it is necessary to determine in some manner the mean or effective value of $dD/d \log E$ for the portion of the characteristic curve to which the evaluation is to apply. This could be accomplished by using over-all gradient, obtained by dividing the density scale by the exposure scale. This procedure, however, is not logical or in accordance with the knowledge of visual perception. When observing a print consisting of a large number of areas differing in brightness, the impression of contrast is based upon the rate of transition from one density to another. It is necessary, therefore, in evaluating the rate factor of contrast to use the average gradient based on density instead of exposure. The contrast may be expressed in terms of sensitometric characteristics as:

$$\Omega = \frac{(D_{max} - D_{min}) \cdot [\bar{G}(D)]}{l\Delta D^2},$$

in which $\bar{G}(D)$ is the average gradient computed in terms of equal density increments and $l\Delta D$ is the smallest density difference which the eye can distinguish. Since this is a constant it can be omitted in the calculation of relative contrast.

The measurement of the contrast of a paper may be accomplished graphically by plotting the gradient, $G = dD/d \log E$, as a function of density. The final value of contrast is, then, the product of the extent factor and the rate factor. The values of *G*, corresponding to various values of density, can be read directly from the first derivative of the *D*, log *E* curve. An example of such a curve is shown in Figure 235. Curve *A* is obtained by plotting gradient as a function of density. Now,

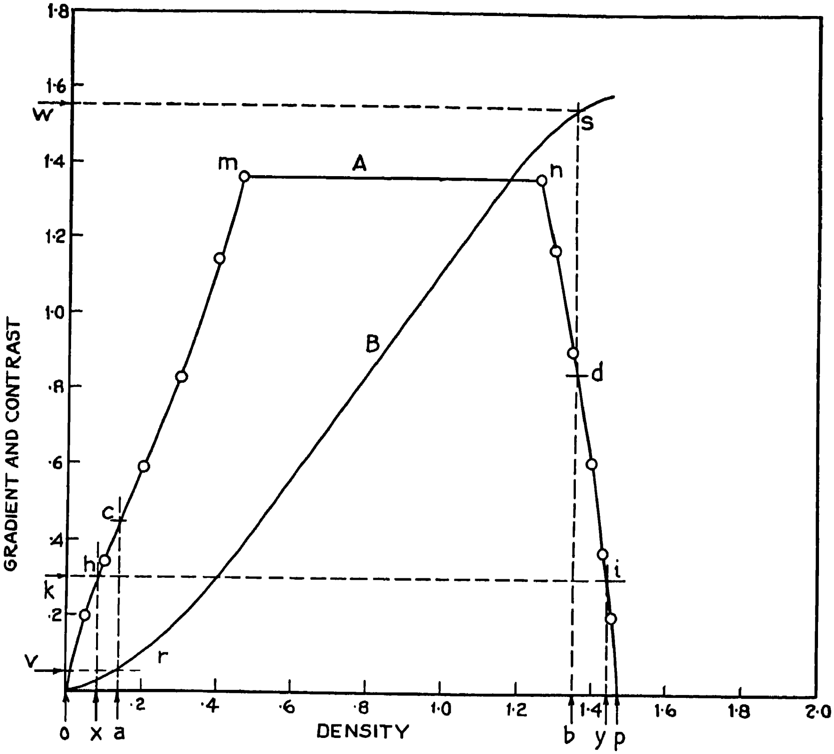

FIG. 235. Curve of contrast as a function of density.

by measurement of the area enclosed by the curve *omnp* and division by the length of the line *op*, the average gradient evaluated with respect to equal increments of density is obtained, giving the rate factor of contrast. The area enclosed by the curve *omnp*, however, is the product of this average gradient and the density interval ($D_{max} - D_{min}$), and hence the area itself gives contrast directly. By integration of the curve *omnp*, the curve *B* is obtained, which shows contrast as a function of density. To determine the value of contrast between any designated points on the characteristic curve, it is only necessary to read the values of the ordinates of curve *B* at the specified density limits and subtract the smaller from the larger.

For practical purposes, it is convenient to establish a scale such that the values lie between 0 and 100, and this can be done by the application of a suitable factor to the values obtained from the curve. In the following table are given the results for a small group of printing papers used for amateur negatives, all of them having the same semimatte surface:

TABLE LXXIV

				Relative Contrast			
Grade	$D_{\max}$	*Exposure Scale*	γ	*Extent Factor Density Scale*	*Rate Factor Mean Slope*	*Contrast*	*Practical Contrast Factor*
Soft	1.40	1.63	1.13	1.34	0.96	1.28	25
Medium	1.40	1.40	1.37	1.36	1.01	1.37	27
Hard	1.48	1.01	2.29	1.43	1.54	2.20	44
Extra hard	1.41	0.81	2.62	1.37	1.85	2.53	50

An instrument for determining the contrast directly from the characteristic curve was designed by Morrison[19] (Figure 236). As the operator scans the curve with the viewing head, *H*, the slope of the curve for each unit of the density scale is measured; and the area of the curve of gradient plotted as a function of the density is integrated. At the end of the scanning cycle, the value of Ω (contrast) appears at the index of the scale drum of the planimeter, which is incorporated in the instrument. The principle of the meter is illustrated in Figures 236 and 237, which are similar in viewpoint and lettering. A small portion of the sensitometric curve *D* is viewed through a biprism, *B*. When the line dividing the two faces of the prism is normal to the part of the curve under observation, the curve appears discontinuous. Then, the position of the prism is adjusted to make the curve appear continuous; the angular displacement of the arm *A* will measure the tangent of the curve at that point. The mechanism in the viewing carriage, *H*, converts the angular displacement of the arm *A* into a linear displacement of *R* proportional to the tangent of the curve. As the prism tube and slotted arm *A* rotate, the roller *R* within the slot is so held that it can move only in the direction *EW*. When the axis of the slot is coincident with the line *CC*, the roller *R* occupies the position *P*. This position corresponds to the setting for zero slope of the curve, and the prism is adjusted to show the abscissa as a continuous line. For any other position, the side *TP* of the triangle *TRP* (Figure 237) is constant. Angle *RTP* is a

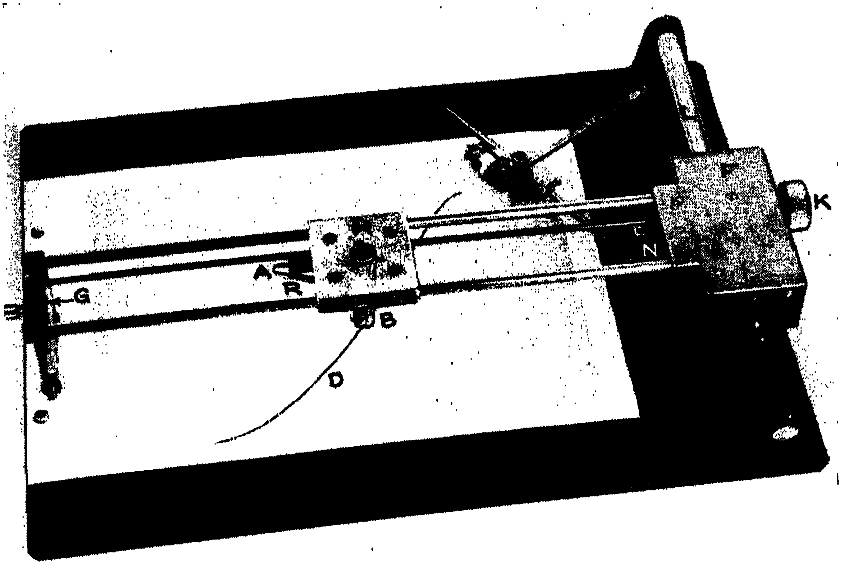

FIG. 236. Contrast meter for photographic papers.

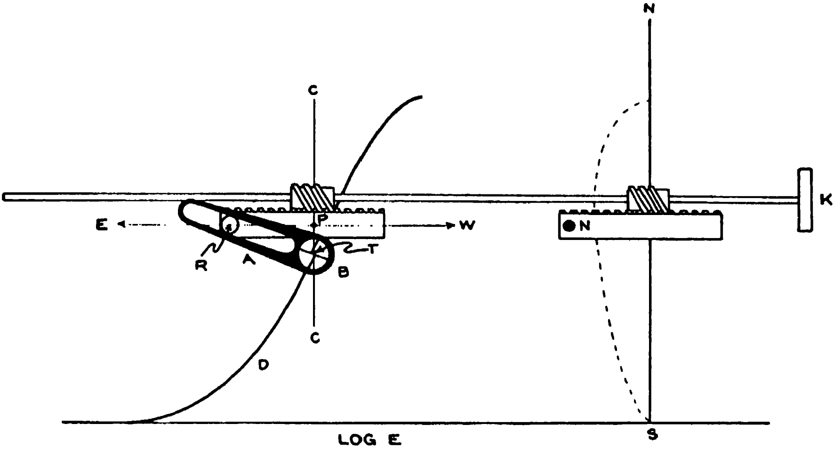

FIG. 237. Diagram of contrast meter.

measurement of the slope of the curve D at point T with respect to the abscissa when the curve appears continuous in the field, and, since $\tan RTP = RP/TP$ and TP is constant, RP is proportional to the tangent of the angle. The value of the tangent is therefore measured by the displacement along EW of R from P. The rotation of the prism is controlled by the knob K acting through the shaft, worm, and rack. The worm is keyed to rotate with the shaft in such a manner as to provide freedom of motion along the shaft. This lateral motion causes no mechanical movement of the rest of the system but enables the curve D to be followed with the prism B. At the right end of the shaft, and enclosed in the large housing F, another worm is fixed to the shaft. This worm and its rack are duplicates of the pair in H. The distance from the NS axis to the point N to which the tracer head of the planimeter is attached corresponds with the displacement of the roller axis R from P. A typical path followed by N, when the curve is scanned, is shown by the dashed line. This line represents the derivative curve plotted as a function of density. After the curve is scanned and the planimeter head is returned to the position S, the area under the dashed-line curve is indicated by the planimeter drum index. This area multiplied by an appropriate factor gives the value of contrast on the desired scale.

To simplify the computation of the value of Ω, F. and A. Urbach[20] suggest that an approximation to Jones' measurement of contrast is given by the equation

$$\Omega = \frac{(D_s{}^3 \cdot \gamma_{\max})^{\frac{1}{4}}}{(\log E_s)^{\frac{1}{4}}},$$

where D_s is the density scale and E_s the exposure scale between the points where the gradient = 0.2. A test of this formula shows a correlation coefficient of 0.997 with the results given by the expression derived by Jones.

THE EFFECT OF DEVELOPMENT ON THE CURVES OF PHOTOGRAPHIC PAPERS

Inasmuch as developing-out papers almost always contain either free soluble halide or have bromide added to the developer, the effect of the time of development may be expected to be parallel to that for negative materials when the developer contains bromide; thus, not only will the slope increase, but the whole curve will move to the left on the log E axis, the inertia shifting toward a limit reached with extended development (Chapter XI, p. 413). This shift of the inertia or *regression of the inertia*, as it is termed, is characteristic of development in

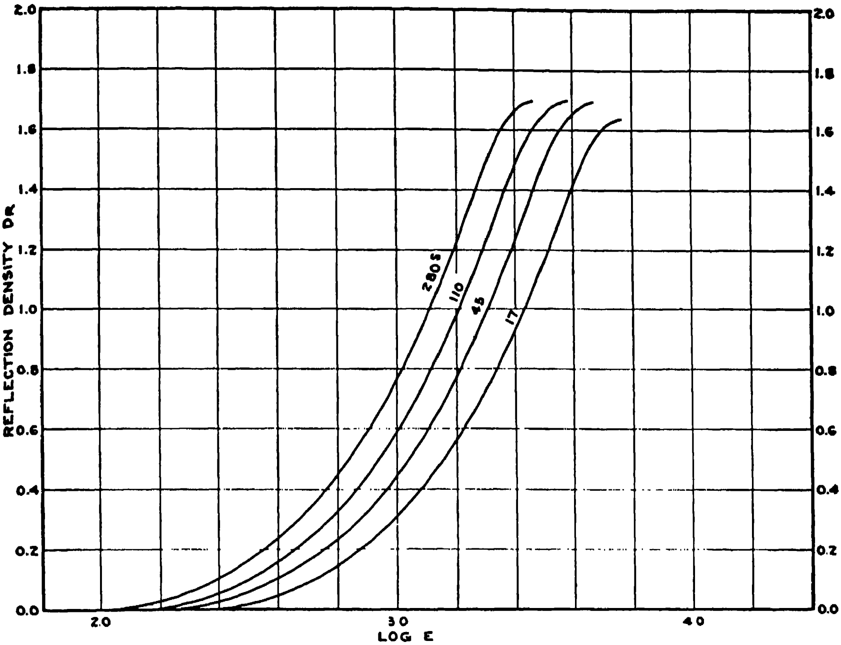

FIG. 238. Effect of increasing development on the characteristic curve of a chloride paper.

the presence of soluble halide. When the velocity of development is very great and much bromide is present, γ_∞ is reached very rapidly, and the effect of development is shown only by a movement of the curve parallel to itself; that is, by regression of the inertia alone. Two typical effects may therefore occur in bromided development: In the one, regression of the inertia occurs simultaneously with increase of slope; and in the other, the increase of slope occurs rapidly at the beginning of development, and thereafter the time of development affects only the regression of the inertia point, this being characteristic of emulsions having very high velocity constants of development.

The rapidly developing chloride and chlorobromide papers used for the printing of amateur negatives present a simple case of parallel curves showing only regression of the inertia with time of development after the initial stage. This is well illustrated in Figure 238. With bromide paper, the results are similar to those obtained with negative materials; the slope increases simultaneously with the regression of the inertia, as shown in Figure 239.

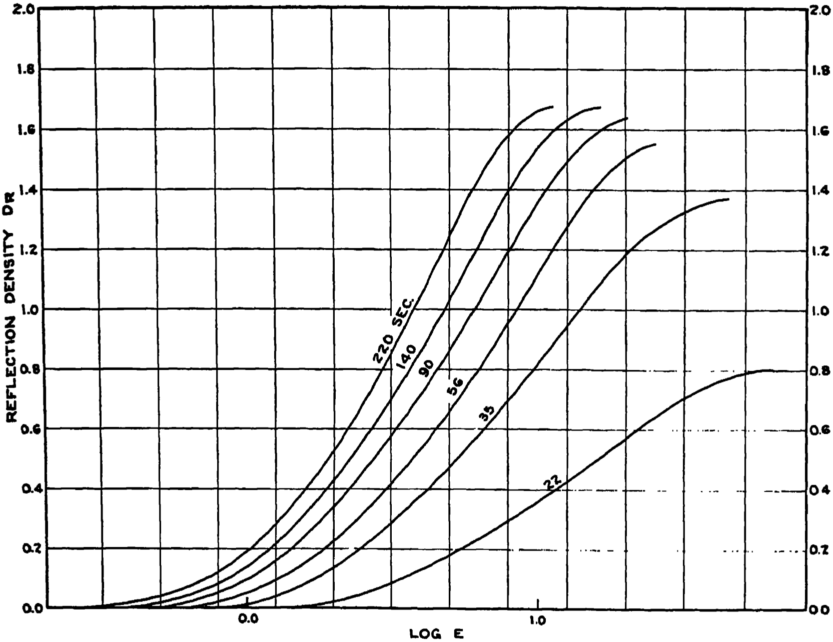

FIG. 239. Effect of increasing development on the characteristic curve of a bromide paper.

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PART V

PHOTOGRAPHIC PHYSICS

CHAPTER XX

THE THEORY OF TONE REPRODUCTION

Tone reproduction is concerned with the determination of the precision with which the photographic process is capable of producing a satisfactory representation of the brightness aspects of the original on a two-dimensional surface.

For the sake of simplicity, it is desirable to differentiate between the two major aspects of the tone-reproduction problem as a whole. By physical methods, it is possible to determine the fidelity with which the brightness and brightness differences in the original are rendered in the reproduction. This constitutes the *objective* phase of the problem. However, an evaluation of the faithfulness with which the *appearance* of the original is reproduced by the graphic representation necessitates a consideration of the psychological relationships involved in sensory and perceptual processes. This is the *subjective* phase of the problem.

In Figure 240 is shown a pictorial diagram[1] illustrating in a qualitative way the various factors involved in a complete solution of the tone-reproduction problem. It is divided into ten steps, I to X. Eight of these, II to IX, inclusive, comprise the objective phase, while I and X indicate the nature of the subjective aspects of the problem. The small black cross, I, represents the *object in consciousness* (the subjective object). A complete solution of the tone-reproduction problem involves the comparison of the characteristics of this object with those of the reproduced object in consciousness, X.

In a study of the purely objective phase, the object, II, may be considered as the starting point. The black cross, illuminated by the sun, is used as a representation of the object, II. A lens forms an image, III, of this object on the light-sensitive material. If this image is allowed to act for the time t_x, a latent image, IV, is formed in the sensitive layer of the negative material. After development and fixation, the latent image is converted into a real image; and the negative, V, is obtained. An image, VI, of this negative is now formed on the positive photographic material by means of a lens or by contact printing. If this image is allowed to act for the time t_y, a latent image, VII, is produced, which is converted by development into a real image

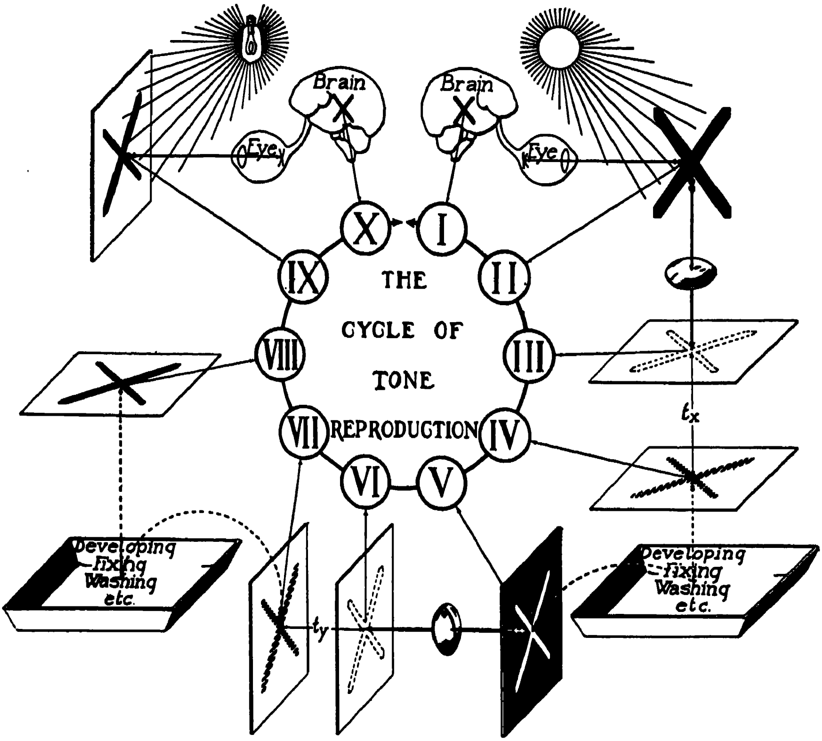

FIG. 240. Diagram illustrating the photographic reproduction of tone.

and thus the positive, VIII, is obtained. The illuminated positive, IX, now becomes the final product of the objective phase of the tone reproduction process. The brightness characteristics of this illuminated positive may now be compared with those of the original illuminated object, II. Such a comparison provides direct information as to the perfection with which the photographic process has reproduced the brightness characteristics of the original.

In Figure 241 is shown a schematic diagram similar to that shown in Figure 240, but more specific. In the small circles are the ten steps in the process corresponding to the pictorial representation of Figure 240. The radial line from each circle connects with an enclosure in which is a statement of the essential characteristic of that particular element. Thus, the essential data relative to the object, II, are the values of the brightness,

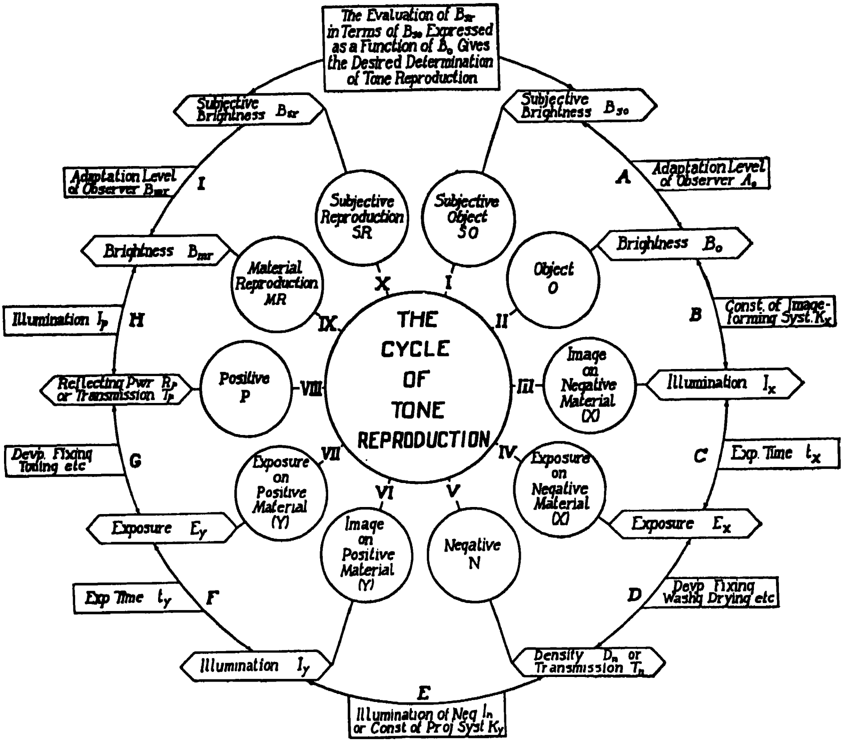
The Evaluation of B_{sr} in Terms of B_{so} Expressed as a Function of B_o Gives the Desired Determination of Tone Reproduction
Subjective Brightness B_{sr}
Subjective Brightness B_{so}
Adaptation Level of Observer B_{mr}
I
Adaptation Level of Observer A_o
A
Subjective Reproduction SR
Subjective Object SO
Brightness B_{mr}
Material Reproduction MR
X
I
Object O
Brightness B_o
Illumination I_p
H
IX
THE CYCLE OF TONE REPRODUCTION
II
B
Const. of Image-forming Syst. K_x
Reflecting Pwr R_p or Transmission T_p
Positive P
VIII
III
Image on Negative Material (X)
Illumination I_x
Devp. Fixing Toning etc
G
VII
IV
C
Exp. Time t_x
Exposure on Positive Material (Y)
VI
V
Exposure on Negative Material (X)
Exposure E_y
Exposure E_x
Image on Positive Material (Y)
Negative N
Exp Time t_y
F
D
Devp Fixing Washg Drying etc
Illumination I_y
Density D_n or Transmission T_n
E
Illumination of Neg I_n or Const of Proj Syst K_y

FIG. 241. Steps in the photographic reproduction of tone.

B_o, of the various object areas. In the enclosures, designated as A, B, C, and so forth, are given the transformation factors by which the data relative to one phase may be transformed into those pertaining to the next. If the brightness values, B_o, of the various areas of the object, for instance, are known, they may be converted into the corresponding image illuminations, I_x, in the camera if the conversion constant of the image-forming system, K_x, is known.

The multiplication of these image illumination values by the exposure time, t_x, indicated at C gives the values of exposure,

E_x, to which the negative material is subjected. To convert these exposure values, E_x, into the density of the various areas of the negative, D_n, information is available in the form of the density-log exposure characteristic for a given negative material processed under specified conditions. Transition from the negative densities, D_n, to the illumination, I_y, incident on the positive material requires a knowledge of the characteristics of the printing system, whether of the contact or projection type. In the contact-printing system, the information required at this point is the illumination incident upon the negative during printing. The printing time, t_y, determines the exposure, E_y, of the positive material. The characteristic density-log exposure function for the positive material processed under specified conditions makes it possible to convert various positive exposures, E_y, into densities, D_p, obtained in the positive after development. If the illumination, I_p, incident upon this positive is known, the brightness of the various areas of the finished positive may be determined; and a comparison of these brightnesses, B_{mr}, with the brightness, B_o, in the original constitutes the final solution of the objective phase of the tone-reproduction problem.

The subjective phase of the problem requires information as to the characteristics of the human observer. This includes the relation between the magnitude of the visual stimulus and that of the resulting sensation, which is commonly referred to as the visual sensitivity to brightness and brightness differences. This visual sensitivity varies enormously, depending upon the previous stimulation of the retina and the characteristics of the entire visual field at a particular moment. The condition of the visual mechanism is usually referred to as the *adaptation level*, A_o. A knowledge of it makes it possible to predict fairly satisfactorily the characteristics of the subjective object, I, these characteristics being expressed in terms of the subjective brightness, *brilliance*, B_{so}. Similarly, the brilliance characteristics, B_{sr}, of the subjective reproduction may be determined; and a comparison of the characteristics of the reproduced object in consciousness with those of the original object in consciousness gives the final desired solution to both the objective and subjective phases of this problem.

The tone-reproduction problem has engaged the attention of many workers in the photographic field. Hurter and Driffield[2] in some of their early work on photographic sensitometry first considered the subject; their treatment was confined to the objective phase alone. Rayleigh[3] also discussed, although rather briefly, the objective phase of the subject. Renwick[4] studied the quality of tone reproduction possible when using the underexposure region of a negative material and later presented a more complete treatment of the entire subject from both the objective and subjective viewpoints.[5] Renwick[6] gave a graphic solution by means of which it is possible to construct the tone-reproduction curve, showing the relation between print densities and object brightnesses. This graphic solution is illustrated in Figure 242.

The logarithms of the object brightnesses to be reproduced are plotted on the base line, *BP*, which represents the magnitude of the brightness scale of the object. The two continuous curves represent the characteristic curves for the positive and negative materials. It is assumed that the intention is to represent the highest density in the negative by zero density in the positive; so that the point *B* of the positive material reproduces the tone corresponding to the point *P* of the original, which, in turn, corresponds to the point *A* on the negative curve. The other points on the required curve can be found by graphic construction. A particular object brightness, *Q*, corresponds to a point *R* on the negative curve. If a horizontal line is drawn through *A*, the vertical distance, *e*, between this line and the point *R* represents the difference between the highest negative density and that at point *R*. When *R* is printed, the positive material receives an exposure greater than that received at the point *B* by an amount of which the logarithm is *e*. If, therefore, a distance equal to *e* is laid off horizontally from *B*, as indicated in the diagram, and a vertical line is drawn to cut the characteristic curve of the positive material at *C*, the density at this point will correspond to the effect of the negative at *R*; that is, to the object brightness, *Q*. A horizontal line drawn through the point *C* intersects a vertical line through the point *Q* at *S*. In this way, one point, *S*, is established on the desired reproduction curve. Every other point may be determined in a similar manner; and the dashed curve, designated as "resulting print," can be established for the specified conditions used in making this graphic solution.

For exact reproduction of the brightness differences in the object, the reproduction curve should be a straight line at an angle of 45° to the base line. Correct proportional reproduction is indicated by a line that is straight but at some angle other than 45°. For instance, enhanced proportional rendering of the tonal scale of the object is indicated by a straight line at angles steeper than 45°, while a proportional compression of the brightness differences of the object throughout the tonal scale of the reproduction is indicated by straight lines at angles of less than 45°. Departure from straightness indicates nonproportional dis-

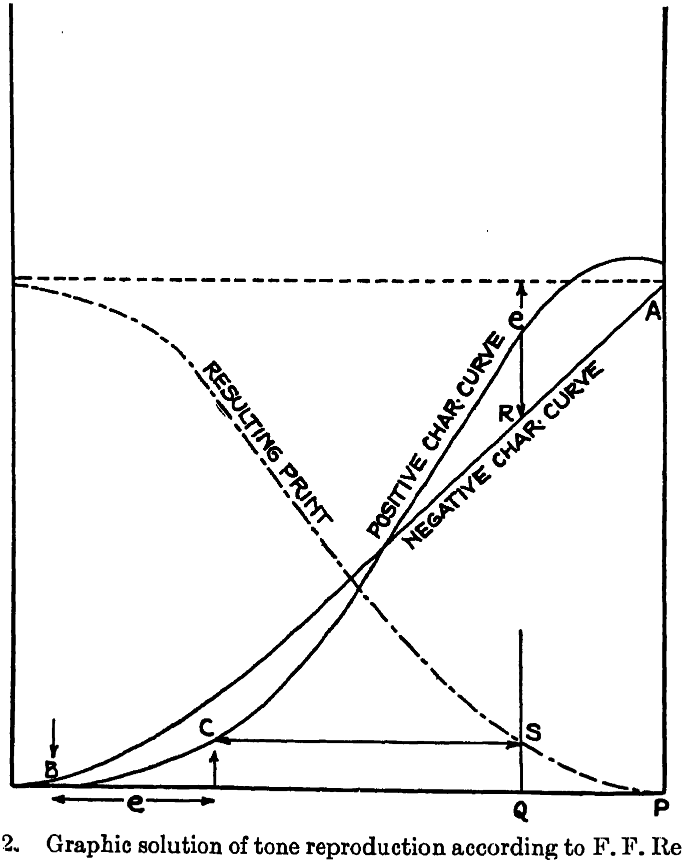

FIG. 242. Graphic solution of tone reproduction according to F. F. Renwick.

tortions of the brightness differences. The gradient at any point on the reproduction curve indicates whether or not at that particular point in the object-brightness scale the brightness difference is enhanced, compressed, or faithfully rendered.

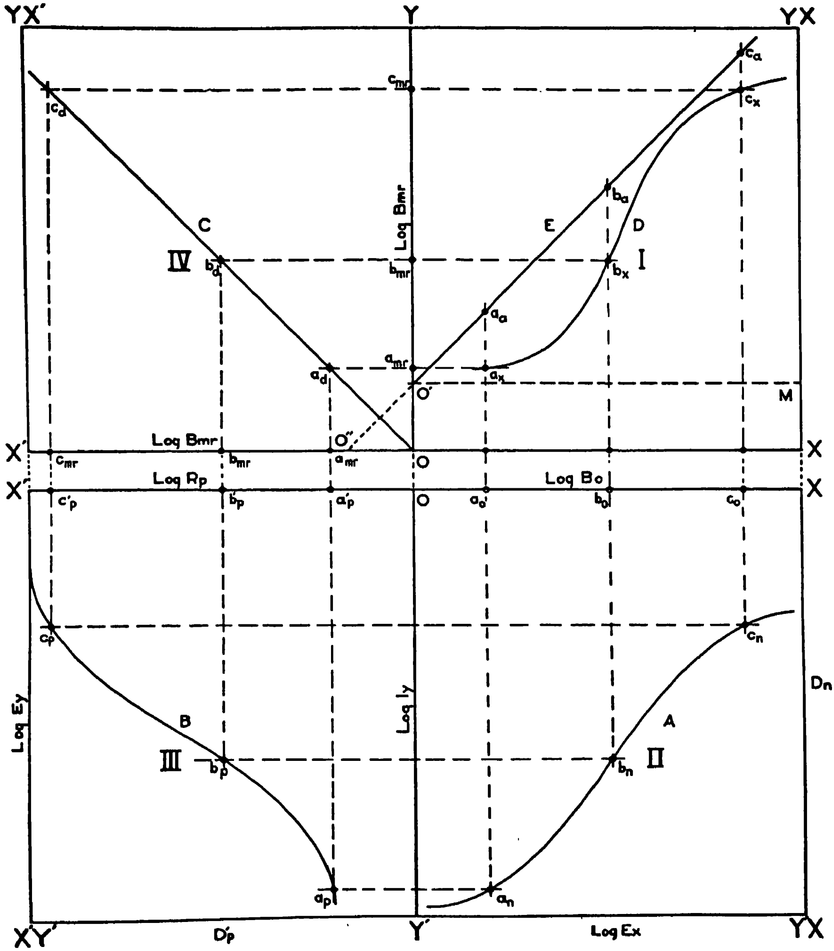

FIG. 243. Graphic solution of tone reproduction according to L. A. Jones.

A graphic solution of the tone-reproduction problem, including both objective and subjective phases, was proposed by Jones.[7] This is a four-quadrant diagram shown in Figure 243. The characteristic curve of the negative material is plotted as curve *A* in the lower right-hand quadrant. At the top of this quadrant is a logarithmic scale of object brightnesses. The adjustment of the log B_o and the log E_x scales to each other is obtained if a density on the negative, such as a_n, falls upon the same vertical line as the logarithm of the brightness of the object area, rendered in the negative by a density of a_n. In the lower left-hand quadrant is plotted the characteristic curve of the positive material. In this case, the logarithmic exposure scale is vertical. The position of the curve, B, relative to the negative curve, A, must correspond to the existing printing conditions. Thus, if the negative density, c_n, is to be rendered by a relatively low positive density, such as c_p, these two points must lie on the same horizontal line. In the upper left-hand quadrant the straight line, C, passes through the origin at an angle of 45°. This diagram applies to a specific case, where the adaptation level of the observer when viewing the illuminated positive is exactly the same as when viewing the original. Under these conditions, the subjective aspects of the tone-reproduction problem are satisfactorily represented by the curve C. Under other conditions, it may be necessary to substitute for curve C as shown a straight line having a slope other than 45° or possibly a curve rather than a straight line.

It is possible now to construct the tone-reproduction curve, D, in the upper right-hand quadrant. For three selected object brightnesses a_o, b_o, and c_o, vertical lines are dropped onto the negative characteristic locating the points a_n, b_n, and c_n. Horizontal lines through these points establish the corresponding points c_p, b_p, and a_p, on the positive characteristic. Vertical lines through these points cut the subjective function, C, at the points a_d, b_d, and c_d. Horizontal lines drawn through these points intersect vertical lines drawn through points a_o, b_o, and c_o, establishing the points a_x, b_x, and c_x; and, with sufficient points, the curve D, the final, desired tone-reproduction curve, can be drawn.

In Figure 244 is shown a construction in which the assumed subjective factors result in a relationship which is not linear. In this case it is assumed that all of the object brightnesses are rendered on the straight-line portion of the curve of the negative material A. The positive material has the density-logarithmic exposure characteristic indicated by curve B. Curve C, in the upper left-hand quadrant, results from conditions in which the adaptation level of the observer when viewing the illuminated positive was very appreciably lower than his adaptation level

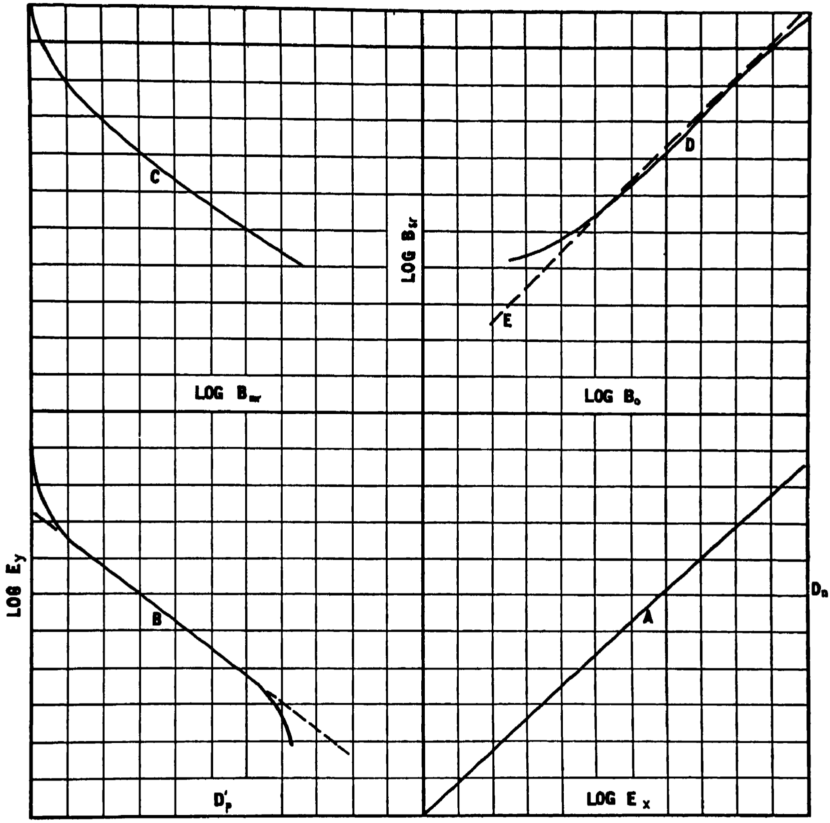

Fig. 244. Tone-reproduction diagram involving nonlinear subjective factors.

when viewing the original. Under these conditions, the final tone-reproduction curve, *D*, has the shape shown.

From tone-reproduction diagrams such as are shown in Figures 243 and 244, some rather interesting and significant analytical relationships may be derived. For instance, if the gradients at corresponding points on the four curves, *A*, *B*, *C*, and *D*, are designated as G_n, G_p, G_z, and G_r, it can be shown that these four gradients are related in the following manner:

$$G_n \cdot G_p \cdot G_z = G_r.$$

That is, the gradient of the reproduction curve at any point is equal to the product of the gradients at corresponding points of the negative characteristic, the positive characteristic, and the subjective characteristic. Since perfect reproduction of brightness differences will be obtained only if the reproduction curve is a straight line at an angle of 45° to the horizontal axis, this condition will be fulfilled only if the product of the gradients of curves *A*, *B*, and *C* is equal to unity. If two of these values are known, it is simple to compute the gradient for the third which will produce a gradient of unity in the reproduction curve. For the straight-line portions of the characteristic curves and of the subjective characteristics, the relationship may be expressed in the form

$$\gamma_n \cdot \gamma_p \cdot \gamma_c = \gamma_r.$$

The subjective aspect of the problem is deferred to a later section.

Returning to Figure 243, the line *E*, drawn at an angle of 45° to the base line in quadrant *I*, is the curve of perfect objective reproduction of brightness differences. For the case illustrated, the reproduction curve *D* starts in the shadow region (low values of $\log B_o$) with a low gradient compared with the line *E*. This indicates that shadow detail is compressed. The gradient of *D* rises for object areas of greater brightness until it is considerably in excess of the ideal curve *E*. Thus, in the middle-tone regions, the brightness differences are enhanced. From this point on, the gradient decreases until, in the extreme highlight, c_x, it is again lower than that of curve *E*, indicating that highlight detail also is compressed. It is obvious that a proper evaluation of the gradients of curve *D* relative to those of curve *E* should provide a quantitative measure of the gradient errors. The magnitudes of these gradient errors as a function of the object brightness are shown graphically in Figure 245, in which the gradient of the reproduction, G_r, is plotted as a function of $\log B_o$. For any point, the ordinate indicates the sign and the magnitude of the gradient error. The average gradient error can be obtained by measuring the area between the curve and the horizontal line *OX* between the points a_0 and c_0 and dividing the value found by $c_0 - a_0$. As shown later, the magnitude of the gradient error is useful in expressing quantitatively the quality of tone reproduction under a given set of conditions.

A tone-reproduction diagram of the type shown in Figure 243 can be used to illustrate graphically some interesting relationships as to the shapes of negative and positive characteristics required for correct tone reproduction. In Figure 246, D has been taken as a straight line corresponding to correct objective reproduction. Curve B in the lower left-hand quadrant is the characteristic curve of a positive material, and the characteristic, A, of the negative material has been calculated so that it gives perfect tone reproduction. Likewise, in Figure 247 a negative characteristic curve is assumed; and the characteristic curve B

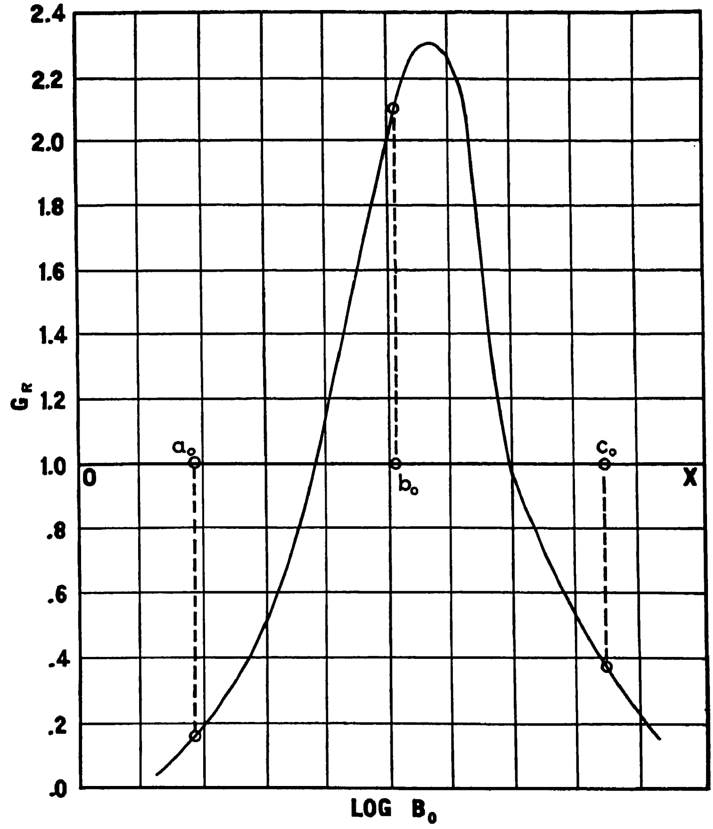

FIG. 245. Gradient errors plotted as a function of object brightness.

of the positive material required for perfect tone reproduction is shown in the lower left-hand quadrant. It is evident that the curves in the lower right-hand and left-hand quadrants of Figures 246 and 247 are mirror images of each other. This condition of affairs may be referred to as the *mirror-image law;* that, for perfect objective reproduction, the negative and positive characteristics must be mirror images of each other, it being understood, of course, that the co-ordinate system in which one of the curves is plotted is rotated through 90° with respect to the co-ordinate system in which the other is plotted. If the negative characteristic is available, it is, therefore, a simple

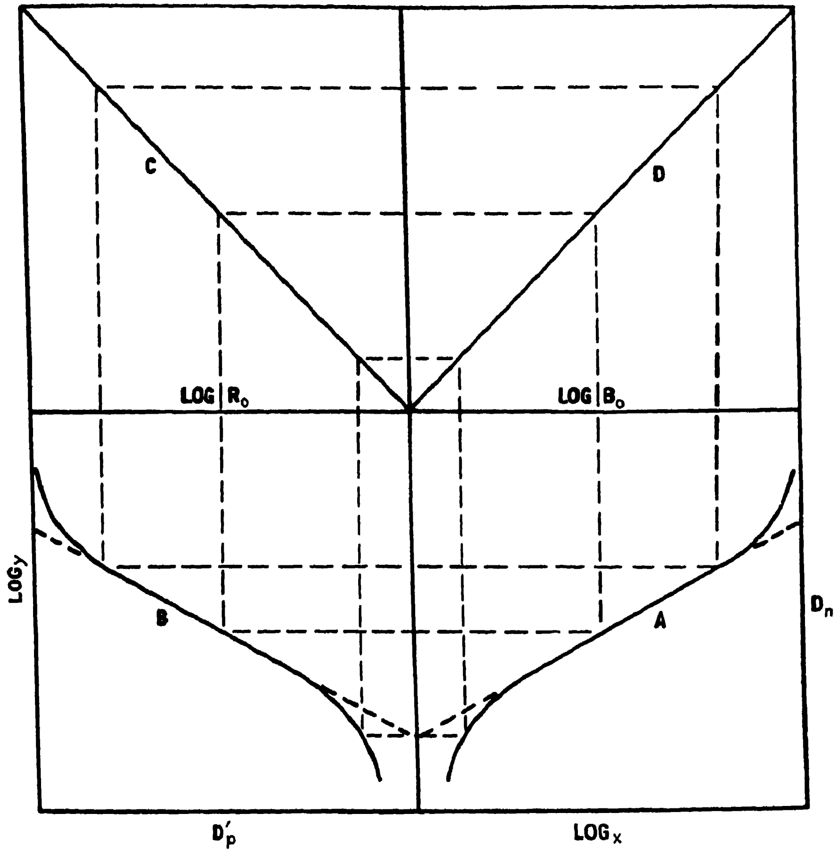

FIG. 246. Tone-reproduction diagram used to calculate the characteristic of a negative material to give perfect reproduction.

matter to determine the shape of the positive characteristic required.

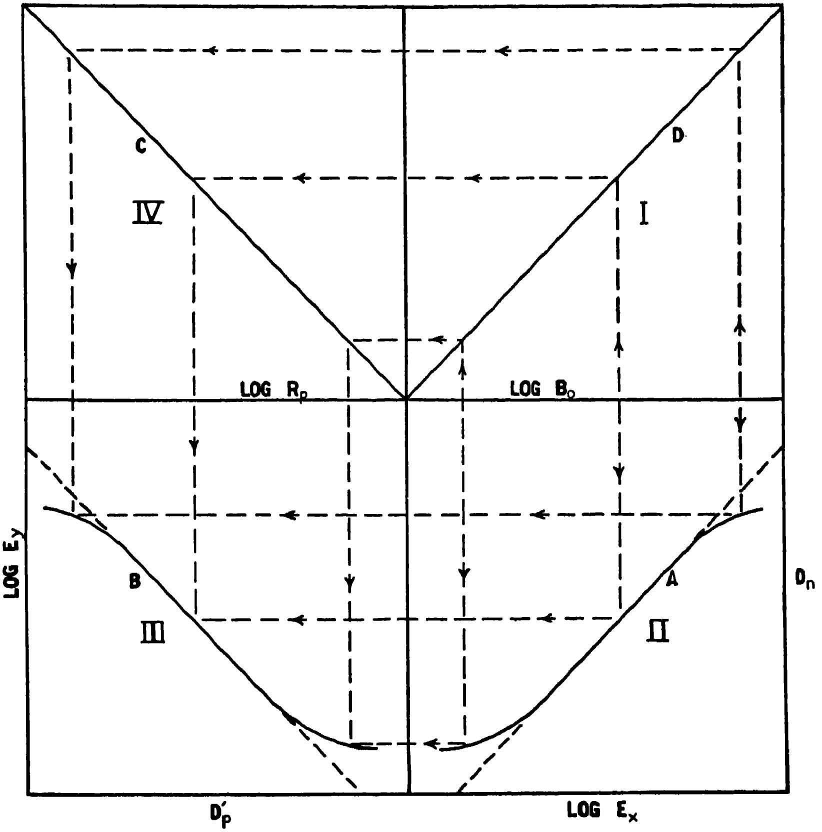

FIG. 247. Tone-reproduction diagram used to calculate the characteristic of a positive material required to give perfect reproduction.

For the objective phase alone, the following analytical relationships are of importance:

The density gradient of curve A (Figure 243) is given by

$$G_n = \frac{d\,D_n}{d \log E_x} = \frac{d \log E_y}{d \log B_o}.$$

Since

$$d \log E_x = d \log B_o,$$

this becomes

$$G_n = \frac{d\,D_n}{d \log B_o}.$$

The density gradient of curve B is given by

$$G_p = \frac{d\,D'_p}{d \log E_v},$$

while for the reproduction curve D,

$$G_{mr} = \frac{d \log B_{mr}}{d \log B_o}.$$

From these relations, it can be shown that

$$G_n \cdot G_p = G_{mr}.$$

To determine the quality of tone reproduction obtainable in practice, it is necessary to consider quantitative aspects, such as the brightness scales, BS_o, of objects, the actual gradients obtainable in various types of negative and positive materials, and the available exposure scales of these materials.

BRIGHTNESS CHARACTERISTICS OF OBJECTS

The brightness of any surface is dependent upon two factors: the reflectance of the surface and the illumination incident on it. Objects differ greatly in reflectance. A surface coated with magnesium oxide or a block of white chalk reflects about 98 per cent of the incident light, while black velvet or black broadcloth reflects one or two per cent of the incident light. A good quality white paper or white cloth reflects approximately 90 per cent of the incident light. Since the brightness scale of an object or scene, BS_o, is defined as the ratio of the maximum to the minimum brightness, it is obvious that the maximum brightness scale that can be realized if all surfaces of objects are illuminated to the same extent is of the order of 90 or possibly 95.

All of the objects composing a landscape or interior scene do not, in general, receive the same amount of illumination. In an exterior scene, certain areas may be in direct sunlight, while others may be shielded from it and even largely shielded from the light from the sky. Thus, objects in the shadow of a building or under dense trees receive much less illumination than those in direct sunlight. It is obvious, therefore, that in such cases much higher brightness scales are to be expected than with objects receiving equal amounts of illumination. If an object having a very low reflectance is in a shadow where the illumination is only 1/100 of that received by an object of high reflectance in direct sunlight, the brightness scale of the scene will be of the order of eight or nine thousand. It is to be expected from these rather general considerations of the subject that the brightness scale of objects may vary over a considerable range.

Hurter and Driffield,[8] in connection with their classical work in the field of photographic sensitometry, concluded from a study of what they considered a representative or average exterior scene that its average brightness scale is approximately 30. Examination of their method for obtaining this value shows that the measurement was made by a photographic method and that what they really measured was the illumination scale of the image in the camera rather than the object illumination scale. In 1922, Goldberg[9] in his excellent monograph on the characteristics of the photographic image stated that a careful search of Eder's Handbook yielded very little important information on this subject but that, according to W. Scheffer,[10] brightness scales as great as 100,000 may be frequently encountered in exterior scenes. Goldberg concludes from his own work that an average exterior scene has a brightness scale of approximately 30. This is based on the average of about 250 scenes. It is uncertain whether this value applies to the average illumination scale incident upon the negative material from a scene of average brightness scale with a camera and lens system having average flare characteristics or whether it applies to the brightness scale measured with a flare-free brightness photometer.

BRIGHTNESS DISTRIBUTION IN EXTERIOR SCENES

A few exterior scenes measured by L. A. Jones with a portable photometer had a brightness scale ranging from 10 to 250. It was estimated, although the number of scenes measured was not sufficient to provide a very satisfactory statistical average, that the average brightness scale in exterior scenes probably lies between 40 and 50. These measurements were made with a telescopic photometer, and it was found later that a small amount of flare light (p. 778) was present which, while of small absolute magnitude, was sufficient to affect the brightness of small

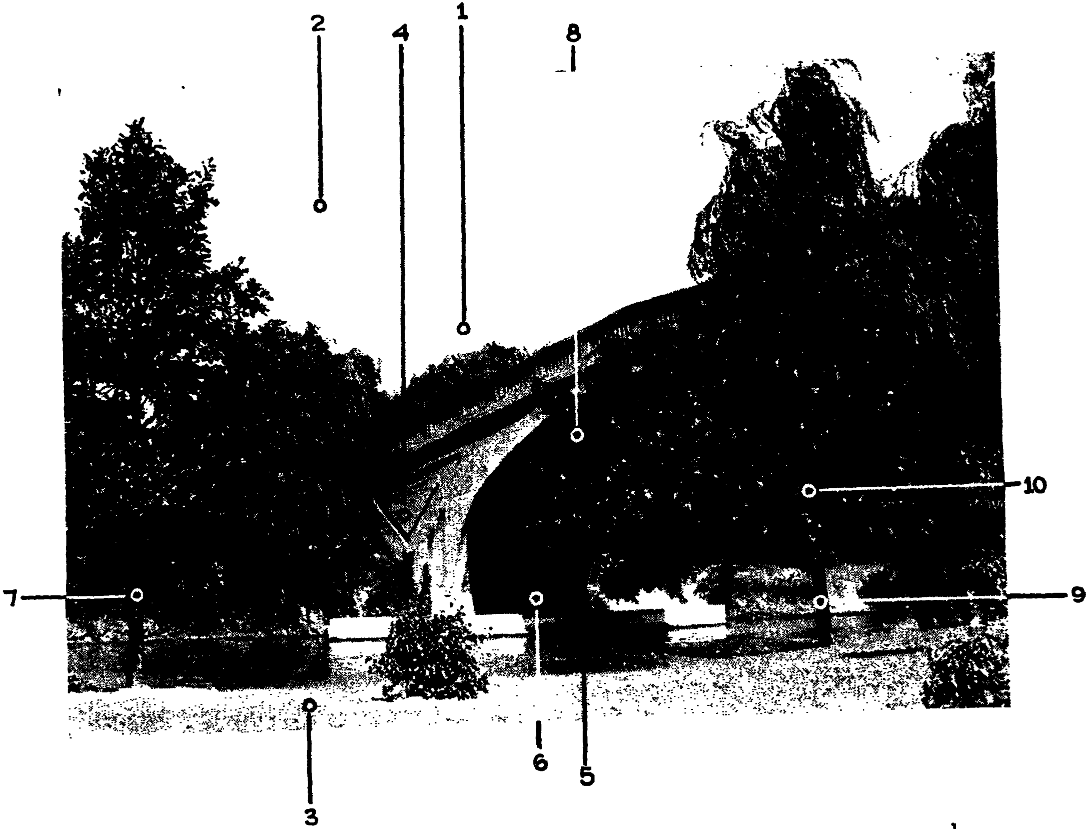

FIG. 248. Landscape scene in which the brightness values were measured.

dark areas surrounded by relatively large areas of high brightness. The estimated average is therefore too low.

Recently, work has been carried out in the Kodak Research Laboratories[26] on a much more extensive scale. A portable brightness photometer, also of the telescopic type, was used; and precautions were taken to reduce flare light to a minimum.

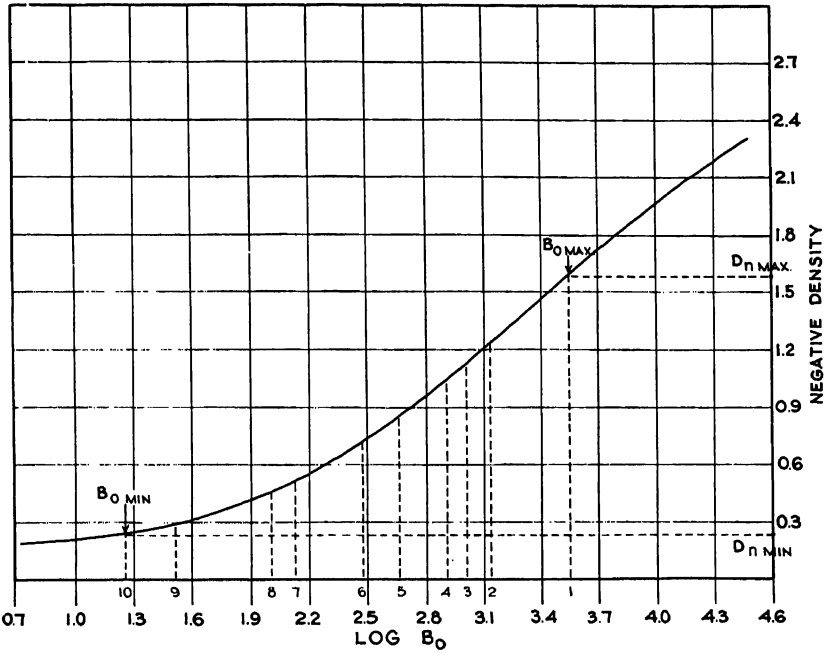

FIG. 249. Density-log exposure curve used to reproduce landscape.

While it is almost impossible to eliminate flare light completely, this instrument when tested seemed to be satisfactorily free from this trouble. About 150 exterior scenes were measured, including a wide variety of subject types over a period of more than a year to include all seasonal conditions, but it is possible that the average may be somewhat higher or lower than that of a similar number of measurements made at widely differing geographical locations. In Figure 248 is shown a reproduction of one of the scenes in which the brightness distribution was analyzed. The small numbered circles indicate the points at which brightness measurements were made, and in Table LXXV are shown the brightness values expressed in foot-lamberts* corresponding to these points. Figure 249 shows the density values by which these various object areas were rendered in the negative. The curve is therefore the effective density-log exposure characteristic of the negative material as used in this particular camera-lens assembly and environment. The curve includes the flare characteristic and differs appreciably from the sensitometrically determined density-log exposure characteristic of the negative material used. This is discussed further in the section dealing with flare light. The maximum brightness in this scene is 3500

TABLE LXXV

BRIGHTNESS VALUES IN AN OUTDOOR SCENE

Area Number	*Description of Area*	*Brightness in Foot-Lamberts*
1	White cloud	3500
2	Blue sky	1350
3	Grass	1000
4	Side of bridge in sun	800
5	Water in sun	460
6	Bridge in open shade	300
7	Tree trunk on left	135
8	Bridge in heavy shade	100
9	Tree trunk on right	33
10	Heavily shaded portion of tree	18
BS_o	Brightness scale of object	195

---

* *Photometric Units.* The unit of luminous intensity is the candle. The two other concepts of greatest importance to the tone-reproduction problem are those of illumination and brightness, the former referring to the amount of luminous flux incident on a surface, and the latter to the amount of luminous flux coming away from a surface.

The unit of illumination used here is the *foot-candle* and is the illumination on a surface of which every point is at a distance of one foot from a point source having a luminous intensity of one candle. The illumination on a surface at any other distance is obtainable by the application of the well-known inverse square law. Illumination may therefore be computed by the following formula:

$$I = L \cdot \frac{1}{d^2},$$

where L = the luminous intensity (in candles) of the source,
d = the distance in feet between source and surface,
and I = the resultant illumination in foot-candles.

The unit of brightness corresponding to the foot-candle is the foot-lambert. A surface which is a perfect reflector and a perfect diffuser, on which the illumination is one foot-candle, has a brightness of one foot-lambert. If a surface is a perfect diffuser but has a reflectance of R, its brightness will be R times the illumination incident on it. If the surface is neither a perfect diffuser nor a perfect reflector, its brightness will be the product of the incident illumination and the directional reflectance factor measured from the viewing angle.

Photographic exposures are customarily expressed in meter-candle-seconds. To convert illumination values expressed in foot-candles into meter-candles, it is necessary to multiply them by the number of square feet in a square meter, 10.76.

foot-lamberts and the minimum, 18 foot-lamberts, the brightness scale being 195.

The summarized results of brightness-scale values for the scenes studied are shown in Figure 250. The average brightness scale for the entire group of one hundred and twenty-six scenes was found to be 160. The observed frequency distribution curve is not symmetrical about this average value, but this lack of symmetry and the presence of what may appear to be secondary maxima are probably due rather to the lack of a sufficiently large number of scenes than to a real lack of symmetry in the distribution of brightness in external scenes.

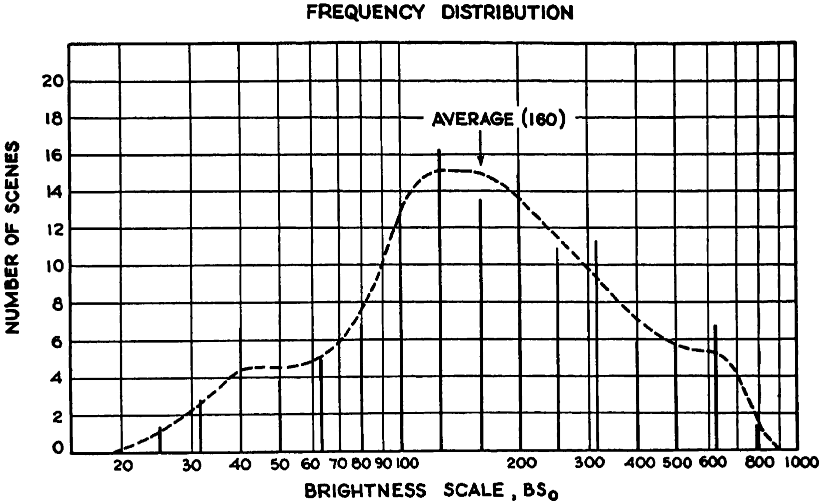

FIG. 250. Brightness scale values for scenes studied.

The one hundred and twenty-six scenes may be classified into a few relatively homogeneous groups based upon compositional and lighting characteristics. Those illuminated by direct sunlight can be arranged into four rather clearly defined groups:

Group 1. This includes distant landscapes and marine and snow scenes. The foregrounds contain no object of interest. Illumination levels, in general, are high and brightness-scale values, low. In many cases, atmospheric haze contributes to the enhancement of the minimum brightness value. Shadows are strong and sharp.

Group 2. The objects of interest are nearer the camera than in Group 1. Foregrounds contain objects of interest. Atmospheric haze is of less importance than in Group 1.

Group 3. The scenes are of the type generally photographed. They include people, gardens, and houses in the foreground, which become objects of chief interest.

Group 4. This is practically identical with Group 3; the only difference is that the objects of chief interest are in shade which is very open. The scene as a whole is sunlit, and, in practically every case, some object in direct sunlight appears in it; but the object of chief interest is shielded from direct sunlight and illuminated by large areas of sky.

Group 5. About twenty-four of the one hundred and twenty-six scenes were photographed under conditions which may be designated as hazy, light clouds or heavy clouds, and which are miscellaneously distributed throughout the distant, remote, and near-by categories. All of them are included in Group 5. The average values of brightness for Groups 1, 2, 3, and 4 have considerable significance as a guide to correct exposure for these groups. The lighting conditions in Group 5 are so diverse that the average has little significance as a guide to correct exposure.

In Table LXXVI are given the average values for the five groups defined above, some scenes being used in more than one group. The first four columns relate to the brightness distribution in the groups, and the last four relate to other characteristics discussed later. It is seen that the average for the minimum brightness decreases progressively in the first four groups. The average maximum brightness also decreases, but at a lower rate. The brightness-scale average increases progressively. It is interesting to note that if the recommended exposure is based upon the minimum object brightness, it will almost exactly double from group 1 to 2, 2 to 3, and 3 to 4. This agrees almost perfectly with the recommendations given in published exposure tables and based upon years of practical experience. In the section at the bottom of this table, under "Average of All Groups," are given the averages applying to the entire group. From this it is seen that on the average the minimum brightness is 14.5 foot-lamberts, while the maximum is 2300 foot-lamberts, giving the average brightness scale of 160 already mentioned.

The brightness scale to be expected in interiors is about the same as that existing in compositions of similar nature out-of-doors. Sets in portrait and motion-picture studios rarely exceed a brightness range of 150; in home portrait photography and in interiors under adverse lighting conditions, brightness scales exceeding this value may frequently be encountered. The logarithm of 160, the average brightness scale found in this work, is

TABLE LXXVI

	1 B_o *min*	*2* B_o *max*	*3* BS_o	*4* $B_o(M)$	*5* IS_i	*6* FF	*7* *ef.* B_o *min*	*8* ΔB
			Group I—28 Scenes					
Min.	20	1500	27	720	18	1.15	54	8.0
Max.	160	11500	285	5700	91	3.30	255	139
Av.	55	4500	81	1650	43	1.90	105	43
Ratio $\frac{\text{Max.}}{\text{Min.}}$	8.0	7.7	10.5	7.9	5.1	2.85	4.7	17.5
			Group II—39 Scenes					
Min.	8.4	820	35	270	22	1.30	20.5	9.2
Max.	76.0	9200	340	3000	155	4.80	165.0	109
Av.	24.5	3150	130	910	56	2.30	56	29.5
Ratio $\frac{\text{Max.}}{\text{Min.}}$	9.0	11	9.7	11	7.0	3.7	8.1	12
			Group III—38 Scenes					
Min.	5.6	620	42	200	29	1.25	12.5	3.0
Max.	31.0	8000	620	2100	290	6.70	80.0	68
Av.	12.5	2400	190	580	80	2.40	30	15
Ratio $\frac{\text{Max.}}{\text{Min.}}$	5.5	13	15	10.5	10	5.4	6.4	22.5
			Group IV—19 Scenes					
Min.	2.0	710	115	53	32	1.25	5.6	1.1
Max.	11.6	4000	750	720	440	8.70	39.0	34.5
Av.	4.6	1600	345	250	135	2.55	11.5	5.9
Ratio $\frac{\text{Max.}}{\text{Min.}}$	5.8	5.6	6.5	13.5	13.5	7.0	7.0	31.5
			Group V—22 Scenes					
Min.	0.82	55	27	38	22	1.15	1.1	0.2
Max.	50.0	3700	640	2300	350	9.50	79.0	65.0
Av.	6.3	1050	165	320	60	2.75	17.5	8.9
Ratio $\frac{\text{Max.}}{\text{Min.}}$	61	67	23.5	61	16	8.3	72.0	295
			Average of All Groups					
Min.	0.82	55	27	38	18	1.15	1.1	0.2
Max.	160.0	11500	750	5700	440	9.50	255.0	139.0
Av.	14.5	2300	160	640	68	2.35	34	17.0
Ratio $\frac{\text{Max.}}{\text{Min.}}$	19.5	210	28	150	24.5	8.3	230	630

2.2. Since the available density scale of a glossy developing-out paper is approximately 1.8, the entire brightness range of an average scene cannot be rendered without some compression. Many exterior scenes have brightness scales which greatly exceed the average value, and in many cases a very considerable compression of the brightness scale must be accepted in photographic reproduction.

CHARACTERISTICS OF IMAGE-FORMING SYSTEMS

To determine the distribution of illumination on the photographic material when a scene of specified brightness composition is photographed, the characteristics of the objective must be known, as well as the relation between the brightness of various elements of the composition and the illumination at the corresponding points of the image. The illumination on the photographic material consists of two parts: one, the image-forming light and the other, the non-image-forming light arising from various sources, such as reflection or scatter at the glass-air surfaces of the lens system, and interreflections within the lens mounting and camera interior. The non-image-forming light is usually referred to as *flare light.* If I_i is used to designate the total image illumination expressed in foot-lamberts; I_{io}, the illumination due to the image-forming light, that coming directly from the object areas; and I_{if}, the image illumination due to the flare light alone,

$$I_i = I_{io} + I_{if}.$$

THE RELATION BETWEEN B_o AND I_{io}

If the brightness of an object area, B_o, is known, the value of I_{io} for a corresponding point in the image formed on the photographic material can be computed by the following formula:

$$I_{io} = B_o \frac{f^2}{4V^2F^2} \cdot \cos^4 \theta \cdot H \cdot T_g, \qquad (1)$$

where I_{io} = image illumination (foot-candles)
B_o = object brightness (foot-lamberts)
f = focal length
V = image distance
d = diameter of stop

$F = f/d$, aperture ratio
θ = angle of image point off axis
T_g = transmission factor due to reflection and absorption by glass
H = transmission factor at points off axis due to vignetting by barrel.

In case the object lies on the axis of the lens, the $\cos^4 \theta$ and H terms in this equation may be ignored; and if the object is at infinity, the equation simplifies to:

$$I_{io} = B_o \cdot \frac{1}{4F^2} \cdot T_g. \tag{2}$$

On the average, however, objects are not at infinity, and a correction should be made for the change in the relationship between I_i and B_o for finite object distance.

Account should also be taken in a practical formula of the loss due to vignetting and the optical loss from the angle subtended by off-axis objects. The weighted average displacement from the optical axis of important objects may be taken as ± 15 degrees.

$$\text{Cos}^4\ 15° = 0.866.$$

In addition, there is a loss from vignetting by the barrel of the lens. This depends upon the design of the lens and the aperture, but for a point 15° off axis this loss may be represented by an average of 25 per cent. Light is lost by reflection at the air-glass surfaces of the lens and by absorption within the glass. On the average, modern lenses, which frequently have six or eight glass-air surfaces, do not transmit more than 70 per cent of the incident light. These various factors, which require consideration in the determination of a probable average value of the relation between I_i and B_o, may therefore be

$\cos^4 \theta = 0.866, \quad \theta = 15°$
$T_g = 0.70$
$H = 0.75, \quad \theta = 15°$
for a finite object distance $\frac{f^2}{V^2} = 0.90.$

By insertion of the values of these four factors in formula (1), the result becomes

$$I_{io} = B_o \cdot 0.409/4F^2. \qquad (3)$$

If it is desired to express I_i in meter-candles instead of foot-candles, the equation becomes

$$I_{io}\,(\text{m.c.}) = B_o\,(\text{ft-L}) \cdot \frac{0.409 \cdot 10.76}{4F^2}, \qquad (4)$$

which reduces to

$$I_{io} = B_o \cdot 4.4/4F^2. \qquad (5)$$

FLARE LIGHT IN THE CAMERA

The non-image-forming light arises from several sources. Light is scattered by flaws in the glass, dust or fingerprints on the surfaces, or imperfections in the surfaces. Even in a lens of clear glass having perfectly clean, smooth surfaces, scattering is caused by reflections from the surfaces in the lens, such as the glass-air surfaces of the lens elements, the inside of the lens mount, diaphragm, and shutter blades.

The most interesting and important case of multiple reflected light in a lens is that from the glass-air surfaces of its elements. Goldberg[9] made extensive investigations of the causes of so-called *lens flare* and gives as an example the diagram of a simple meniscus lens shown in Figure 251. Part of the beam passing through the lens to form an image is reflected at the first surface toward the object and need not be considered further. But of the part reflected at the second surface, a fraction is again reflected at the first surface and continues toward the image plane. These reflected beams form images, as shown in the diagram, at *a* for the single reflection, and *b* for the double reflection. Thus, every pair of glass-air surfaces in a lens constitutes an image-forming system sending light in the direction of the primary lens image. The number of secondary images increases rapidly with the complexity of the lens and equals, in fact, $\frac{N(N-1)}{2}$,

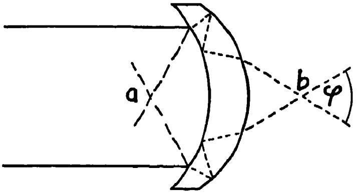

FIG. 251. Diagram showing flare in a simple meniscus lens system.

in which N equals the number of glass-air surfaces. (Cemented surfaces reflect a negligibly small amount of light.) Thus, in a four-piece uncemented anastigmat lens, there are 28 secondary images; and the addition of a filter increases this number to 45. For several typical lenses having different numbers of glass-air surfaces, Goldberg located all these secondary images and measured their aperture angles. For the most part, the images fall at large aperture angles near the lens; so their beams upon reaching the film plane are spread out and of low intensity. In pictures of a bright light against a dark background, an image formed near the focal plane, however, usually appears as a rosette and constitutes a serious lens fault. A more frequent occurrence is the formation near the focal plane of images of the diaphragm. These are particularly noticeable at small apertures because the brightness of the primary image decreases, while only the size and not the brightness of the diaphragm image is reduced.

Since the reflectivity of a glass-air surface is ordinarily about 4 to 6 per cent, depending upon the refractive index of the glass, and at least two reflections are required to direct the light toward the focal plane, the intensity from a secondary image at the film plane cannot exceed approximately 0.0036 that of the primary image, and such an image can become apparent only in scenes having high contrast. The total light from all the secondary, tertiary, and lesser images, however, often seriously degrades the primary image. If there are N surfaces having a reflectivity r, assuming all transmitted light reaches the focal plane, the amount of true image-forming light reaching the image plane will be proportional to $(1 - r)^N$. The amount of non-image-forming light reaching the film plane, owing to multiple reflections among the surfaces, will be proportional to $\frac{1 - r}{1 + (N - 1)r} - (1 - r)^N$. The ratio of these quantities is an approximate measure of the scattered light level to be expected. In a four-piece uncemented anastigmat lens, this ratio is 0.06 (assuming $N = 8$, $r = 0.05$). No part of the image, therefore, will have a brightness less than 0.06 the average brightness, even if the corresponding part of the original scene has a zero brightness.

The reflectivity of glass can be reduced[11] by applying to its surface a thin layer of transparent material having a refractive index intermediate between that of air and glass. For the maximum effect, this layer should have a refractive index equal to the square root of the index of the glass and an optical thickness of one-quarter the wave length of green light. With such a layer, the reflectivity for green light at normal incidence is zero and the average reflectivity for all colors is reduced to about one-half of one per cent. Thus, treatment of the four-piece uncemented anastigmat lens should increase its transmission from 66 to 96 per cent and decrease the scattered-light ratio from 0.06 to 0.0007. This transmission is not attained in practice, and the calculations are only approximate because the effects of the interior of the lens mount, edges of the lens elements, shutter, diaphragm blades, and bellows have been neglected.

For complete experimental information about the scattering properties of a lens, the light distribution should be measured from a point source for each angle of incidence throughout the film plane. A much simpler method, due to Goldberg, gives a single integrated value of considerable significance as regards the light-scattering characteristics of a lens. This is illustrated in Figure 252. The interior surface of the hemisphere, *a*, is illuminated to a high level by a group of incandescent lamps, *g*. At the pole of this hemisphere is located a small opening in the enclosure *b*, which is blackened and diaphragmed, so that the brightness of the aperture as viewed from the lens position, *O*, is extremely low; *b*, in fact, serves as a black body test spot. The objective under test, *O*, forms an image of the black body test spot and its brightly illuminated surroundings on a photographic plate at *P*. By the methods of photographic photom-

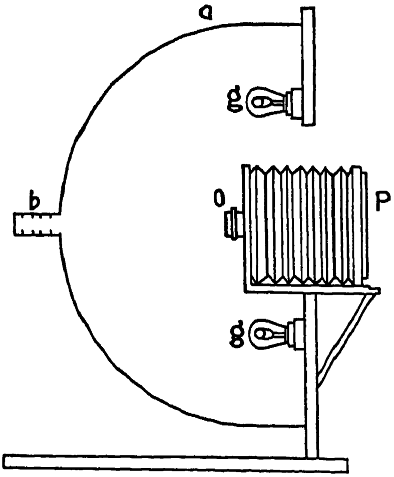

FIG. 252. Method of measuring the light-scattering power of a lens.

etry, the illumination in the image of the black hole and in the image of the bright surrounding field is determined.

The ratio of the maximum to the minimum image illumination is termed by Goldberg the *specific brilliance of the lens.* Actually, this number represents the maximum image illumination scale, IS_i, which under this particular set of conditions can be obtained with the lens under test. This number is of considerable value in classifying different lenses among themselves with respect to their light-scattering characteristics. The specific brilliance, however, is not of much value in determining the relation between the brightness scale of an object (or scene) and the illumination scale of the image for conditions other than those of the test, and it is of little value for tone-reproduction computations.

TABLE LXXVII

Type of Lens	*Number of Glass-Air Surfaces*	*Specific Brilliance*
Meniscus Achromat	2	160
Double Anastigmat	4	63
Triplet Anastigmat	6	31
Four-lens Anastigmat	8	16
Four-lens Anastigmat with Filter	10	10

In Table LXXVII are given the values obtained by Goldberg for the specific brilliance of some of the objectives which he investigated. As the number of free glass-air surfaces increases, the specific brilliance decreases rapidly.

Goldberg also measured the specific brilliance of a group of lenses when the black body test spot was placed at various angles to the optical axis of the lens. The results are shown in Table LXXVIII. In general, the value of specific brilliance increases rapidly as the off-axis angle increases, indicating that the flare light is not distributed uniformly over the focal plane, although this conclusion does not agree with statements at other points in Goldberg's monograph.

For the uniform distribution of reflected light, it is possible to compute the flare due to any number of glass-air surfaces. Tuttle and White[12] give the ratio of reflected light to directly transmitted light as

$$\frac{I_R}{I} = r^2\left\{1 + \frac{1}{1 - t^2}\left[2(n - 1) - \frac{t^4(1 - t^{4(n-1)})}{1 - t^2}\right]\right\},$$

where I_R = light transmitted after reflection at back and front surface of plate

I = directly transmitted light

$r = \left(\frac{u - 1}{u + 1}\right)^2$ = Fresnel reflection coefficient (u = refractive index)

$t = \frac{4u}{(u + 1)^2}$

n = number of surfaces.

This formula assumes normal incidence and neglects reflected light of higher order and optical absorption within the glasses.

TABLE LXXVIII

BRILLIANCE OF THE OBJECTIVE

	Angle			
	0°	*10°*	*20°*	*30°*
Meniscus Achromat				
$f/6.8$ without mount	200	320	400	630
with front diaphragm $f/12$	100	125	100	80
Double Anastigmat f/6.8 cemented				
$f/6.8$	100	125	160	200
$f/18$	80	100	200	500
Triple (Cooke lens) f/6.8				
$f/6.8$	40	50	63	80
$f/18$	32	63	100	125
Uncemented Anastigmat f/6.8				
$f/6.8$	20	25	50	63
$f/18$	12.5	20	63	160
$f/6.8$ with filter	16	20	32	40
Meniscus Achromat f/6.8				
clean	200	320	400	630
with large fingermarks	40	250	400	500
dusty	40	100	160	160
with slight film of moisture	32	50	100	160
with heavy film of moisture	16	10	50	50

If, further, it is assumed that all of the light reflected at the glass-air surfaces is uniformly distributed and that all of it strikes the primary image, the specific brilliance for a lens system containing various numbers of free glass-air surfaces should be as follows, N being the number of free glass-air surfaces:

N	*Specific Brilliance*
2	625
4	108
6	48

These values are considerably higher than those given by Goldberg, as shown in Table LXXVII. It seems possible, therefore, that either the flare light of the objectives measured by Goldberg was not actually uniformly distributed or that other factors contributed to the amount of flare light and reduced the values of specific brilliance. The sensitometric methods used in measurements of specific brilliance are laborious, but photoelectric instruments have been designed so that the grading of lenses for contrast rendition can be made a routine matter.

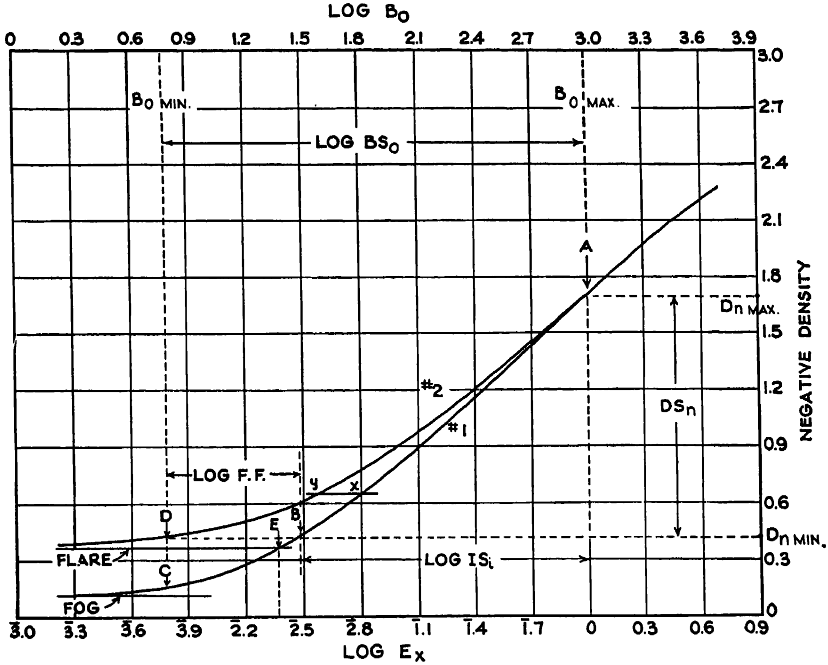

FIG. 253. Diagram for the valuation of total camera flare.

A method of evaluating total effective camera flare for a particular set of conditions is illustrated in Figure 253. The data required for the solutions of this problem include the values of maximum and minimum object brightness, the corresponding maximum and minimum negative densities, and the characteristic curve for the negative material on which the photograph is made. Curve 1 represents the characteristic for the negative material. Values of maximum and minimum negative densities are located as shown on the density scale at the right and correspond to points A and B on the curve. The scale at the top of the figure is used to lay out the log brightness scale of the object. The maximum value of object brightness is placed at the point where a vertical line through the point A cuts the $\log B_o$ scale. A vertical line dropped through $B_o$min cuts the characteristic curve 1 at the point C. The ordinate of this point C is the negative density by which the minimum object brightness would have been rendered had no flare been present when the photograph was made. Actually, the ordinate of point B is the negative density corresponding to the minimum object brightness. It is evident from this that curve 1 is not the effective operating characteristic of the negative material and image-forming system used. Such a curve, however, can now be constructed. A horizontal line through the point B intersects a vertical line through C at the point D, and this point must lie on the effective printing characteristic of the negative. This characteristic is practically coincident with the sensitometric characteristic at the point A since the illumination due to flare light is always small compared to the image illumination corresponding to the area of maximum object brightness. By simple geometrical or graphical principles, curve 2 can be constructed and gives the relation between negative density and logarithmic object brightness, $\log BS_o$, which must be used in the solution of tone-reproduction problems. The distance along the $\log E$ axis between points B and D, $\log F.F.$, is a measure of the magnitude of the flare. This is the number by which the measured value of object-brightness scale, BS_o, must be divided to obtain the image-illumination scale IS_i,

$$\log BS_o - \log FF = \log IS_i.$$

Incidentally, the value of the flare factor found in this way is also useful in determining the effective minimum limiting gradient for the printing characteristic. This, of course, is the gradient at point D. If the gradient at point B of the negative characteristic curve is known, that value divided by the flare factor will give the gradient at point D.

A useful concept is to regard the result on the image plane as equivalent to the addition of a fixed brightness, ΔB, to all of the object brightnesses, B_o, as observed. Then, the image illumination corresponding to the various object brightnesses, $B_o + \Delta B$, can be computed by using equation (1) relating image illumination and object brightness. This procedure also illustrates a relatively simple method of constructing the desired printing characteristic, curve 2, Figure 253. In Figure 253 $B_o$max is 1000 foot-lamberts, while $B_o$min is 6.25 foot-lamberts, the brightness scale, BS_o, being 160. The flare factor is 5.0. The point B on curve 1 therefore corresponds to a B_o value of 31.25. The subtraction of 6.25 from this gives for this particular case a value of ΔB = 25 foot-lamberts. If any point on the log B_o scale is taken, such, for instance, as 1.8, which is represented on curve 1 by the point x, it is evident that the image illumination resulting from the object brightness, $B_o + \Delta B$, at this point is 63.1 foot-lamberts. By subtraction of the ΔB value from this, the actual object brightness is found to be 37.9 foot-lamberts. The logarithm of this being 1.58, a perpendicular dropped from 1.58 onto the log B_o scale intersects a horizontal drawn through the point x on curve 1 at y, which must lie on the desired printing characteristic. In a similar manner other points can be determined and the complete characteristic drawn in.

The values in the last four columns of Table LXXVI are now seen to be derived from the graphical constructions illustrated in Figure 253. In column 5 are given values of the illumination scale of the image, IS_i, while in the sixth column are values of flare factor. In the seventh column are the values of effective minimum object brightness, and in the last column, those of ΔB. It is to be noted that the average value of the illumination scale of the image increases progressively for the first four groups of scenes, and this is true also of the average value of flare factor. The minimum value of flare factor is about the same for all groups, while the maximum increases rapidly from group to group. In the last section of the table, the average illumination scale of the image is seen to be 68. This represents the exposure range which the negative material is called upon to render on the average. Since the exposure scale of most high-quality negative materials is several hundred, it is obvious that modern negative materials can give satisfactory rendition of the image illuminations. The maximum image-illumination scale observed in this group of subjects was 440, which is only about half of the total negative exposure scale available. It is interesting also that the average value of the effective minimum object brightness decreases progressively from Group I to IV, and here, again, the ratio from group to group is approximately 2. The average ΔB is high for the scenes in Group I, for which the average flare factor is relatively low. The average ΔB for Group IV, on the other hand, is low although this results in a high flare factor. This follows, of course, from the fact that the minimum object brightness in scenes of the type of Group IV is low; and, hence, a relatively small added brightness produces a large reduction in the value of illumination scale in the image.

Flare light in the camera has sometimes been stated to be equivalent to a haze layer between the photographic objective and the object. This is not so, because such a haze layer, in addition to raising the brightness of the dark objects, tends to decrease the brightness of the brighter objects. Flare in the camera does not impair definition in the true sense. It decreases contrast, which may easily be interpreted as definition loss. That flare does not impair definition can be proved by increasing the contrast in making the prints to compensate for the loss due to flare light.

The results given in Table LXXVI were obtained with a lens having only four free glass-air surfaces and a specific brilliance, as defined by Goldberg, of 40, the lens being mounted in a camera of inherently low flare characteristics. The average flare factor, 2.35, obtained for this optical system is probably considerably lower than that which would be obtained from the use of a wide variety of cameras and lenses. The tendency in recent years has been toward the use of relatively small compact cameras equipped with wide aperture lenses often having six and eight free glass-air surfaces. For such equipment, the average value of flare factor is probably not less than 5.0. For an average brightness scale of 160, the illumination scale in the image would be 32. Thus, in addition to the compression of brightness differences in the extreme shadow region due to the negative material, there is an additional reduction to one-fifth of the previous value from the effect of flare. However, this part of the tonal scale is rendered in the positive by the steepest portion of the positive characteristic, and much of this apparent loss in shadow detail is recovered in the positive.

NEGATIVE MATERIALS AND NEGATIVES

From the standpoint of tone reproduction, interest centers in the *shape* of the characteristic curve of negative materials and in a consideration of their available exposure and density scales. The shape characteristics of negative materials may be expressed qualitatively, at least, by a specification of the length of the toe of the characteristic curve. Some materials show long sweeping toes covering a relatively long exposure range, so that the straight-line portion does not begin until fairly high density values are reached. On the other hand, materials of the short-toe type give straight lines beginning at relatively low density values, and the exposure scale covered by the toe regions is quite short. In Figures 254 and 255 are shown groups of characteristic curves representing the approximate extremes of toe lengths in present-day commercial materials. Each figure contains a family of four density-log exposure characteristics obtained by development of these materials to different extents. In Figure 254 the toe region covers a log exposure scale interval of approximately 1.20, while in the material shown in Figure 255 this value is reduced to approximately 0.40. In Figure 254, curve 2 represents a normal amount of development, giving a γ value of 0.81. The point O on this curve is located at the minimum useful gradient point.

If this material is used to photograph a scene having a brightness scale, BS_a, equal to the statistical average of the group of scenes already studied, assuming that a camera lens system having a flare factor of 5 is used, the average brightness scale is 160, which divided by 5 gives 32, equivalent in log units to 1.50. It is evident that under these conditions only a relatively small portion of the available exposure scale of this material is used. In fact, the exposure might be increased without intro-

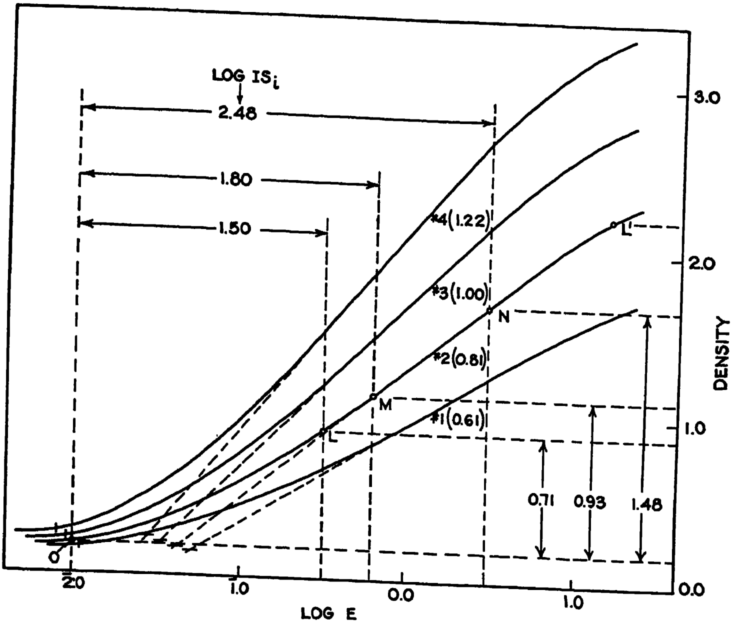

FIG. 254. Group of characteristic curves having long toe portions.

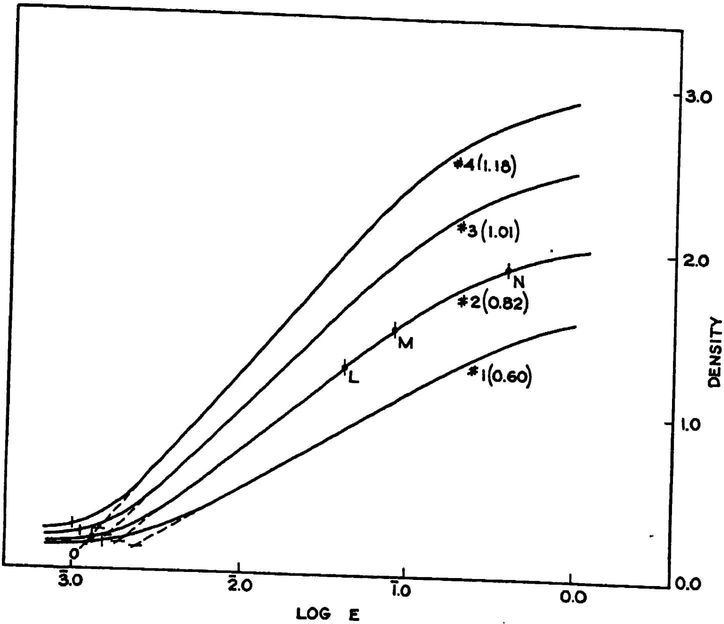

FIG. 255. Group of characteristic curves having short toe portions

ducing any serious loss of highlight detail until the maximum exposure falls at the point *L′*. In this case, the deepest shadow would fall at the point marked *M*, and a negative using only the straight-line portion of the material would be obtained. The exposure would be 32 times that required to render the deepest shadow at point *O*. It is obvious, therefore, that a fairly high latitude is available in making the negative exposure.

Assuming that, instead of a flare factor of 5.0, the camera lens combination has a flare factor of 2.5 and, again, that the deepest shadow is at the point *O*, while the highest image brightness falls at the point *M*. Furthermore, if a scene having the maximum brightness scale of that observed in previous work, namely, 760, is photographed with a camera lens combination having a flare factor of 2.5, by adjustment of the exposure so that the deepest shadow again falls at the point *O*, the area of highest brightness will fall at *N*. Even in this case the exposure could be increased four to eight times without serious loss of highlight detail. It appears, therefore, that in the photography of exterior scenes there is little probability of any conditions being encountered for which the brightness differences cannot be satisfactorily recorded on modern negative materials.

The possibility of transferring the density differences recorded in the negative to the positive material entails consideration of the values of the density scales from various object brightness scales and development conditions. For the three negatives illustrated, namely, *O* to *L*, *O* to *M*, and *O* to *N*, the corresponding density scales are 0.87, 1.07, and 1.62, respectively. According to the tone-reproduction diagram, Figure 243, the density scale of the negative must not exceed the available exposure scale of the positive material if all of the density differences in the negative are to be rendered in the positive material. In general, prints of satisfactory quality will be obtained if the density scale of the negative has approximately the same value as the exposure scale of the positive. To obtain prints from the negatives mentioned above, therefore, it is only necessary to choose positive materials having useful exposure scales of approximately 0.87, 1.07, and 1.62, and these are found in positive materials classified qualitatively as hard, medium, and soft. If the negative represented by *O* to *N* on curve 2 were transferred to curve 4, the density scale would increase to 2.57; and no positive materials have exposure scales of this magnitude. From the standpoint of tone reproduction, therefore, it is necessary to control the development of the negative material in relation to the illumination scale of the image so that the density scale of the negative is printable upon the positive materials.

In Figure 255, negatives resulting from the same conditions as those illustrated in Figure 254 are indicated by the points *O*, *L*, *M*, and *N*. In the case of the material illustrated in Figure 255, the negatives cover largely the straight-line portions of the characteristic curve. Thus, this negative material reproduces the illumination differences incident on the material in the camera with less departure from strict proportionality than in the case shown in Figure 254.

CHARACTERISTICS OF PRINTING SYSTEMS

The next step in the tone-reproduction process is the printing of the negative image onto the positive material. This is accomplished by two general methods—contact printing and projection printing. In contact printing, it is necessary that the density values attributed to the various negative areas are actually the effective densities operative under the conditions used. This is discussed in Chapter XVII, p. 645. In projection printing, the problem is much more complicated. This arises from the diversity in the optical properties of projection printers and from the light-scattering properties of the silver image. Projection printers may be described as diffuse, semidiffuse, or specular. If the negative is placed close to, or in contact with, a sheet of diffusing material, such as pot opal glass, the effective projection density values will be very close to those of the pot opal values. However, if the light incident upon the negative is approximately parallel, as in an enlarger having condenser lenses which image a small light source in the projection lens, much of the light transmitted through the negative is scattered. As a result, the effective projection densities of the negative will be increased. A projection printer employing a light-focusing device, such as condenser lenses or elliptical reflectors, combined with moderate diffusion, such as that afforded by a sheet of ground glass, gives a condition intermediate between the two extremes. In Figure

256, curve *A* shows the relationship for a projection printer having a relatively high degree of specularity, the slope of this line being 0.80.

Projection printers also contribute flare light to the projected image. This has the same origin as flare in camera systems but, in general, the amount in projection printers is very much less than in the negative-making operation. As a rule, the only illuminated area presented to the objective of the projection printer is the negative itself, the surrounding areas being dark. However, particularly in the case of negatives having high density scales, the amount of flare light may be sufficient to produce very definite distortion in the distribution of illumination on the positive material. In Figure 256, curve *B* shows the flare characteristic for the projection printer for which the effect of specu-

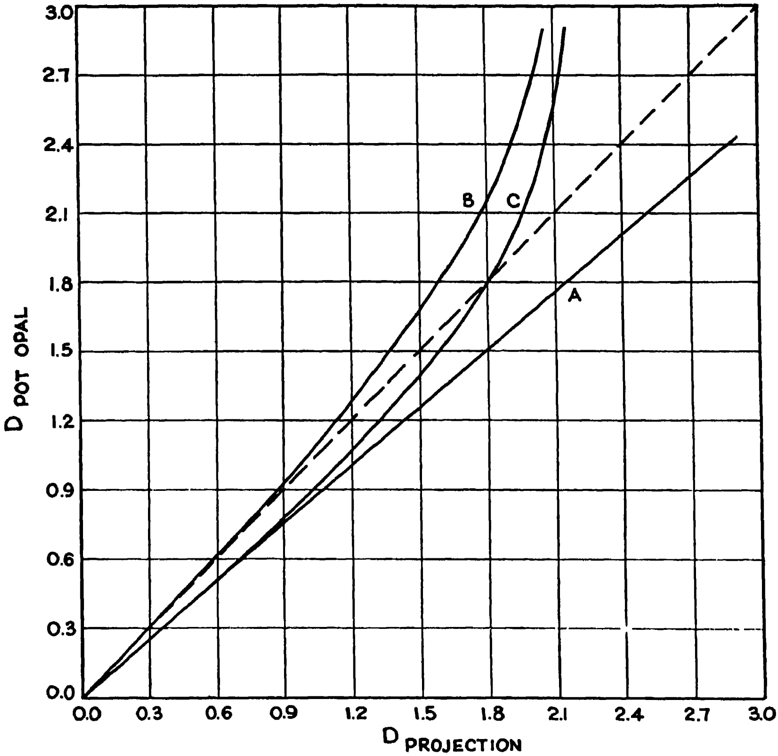

FIG. 256. Operating characteristics of a projection printer.

larity is shown in curve A. The effective operating characteristic of this printer, in which both flare and specularity effects are present, is given by curve C. By the introduction of curve C into an elaborated tone-reproduction diagram, the correct transfer of the negative densities into the image illuminations incident upon the positive material can be achieved.

POSITIVE MATERIALS AND POSITIVES

The characteristics of positive materials are of particular importance from the standpoint of tone reproduction. Modern printing papers fall into three general categories: those referred to generally as chloride, bromide, and chloro-bromide. The first group of printing papers is characterized by high development rates, so that in a few seconds the curve shape has attained equilibrium. With extended development, the curve merely moves parallel to itself along the log exposure axis. Bromide papers develop somewhat more slowly and therefore afford a greater control of curve shape. The chloro-bromide group lies intermediate between the first two but resembles the chloride papers more closely.

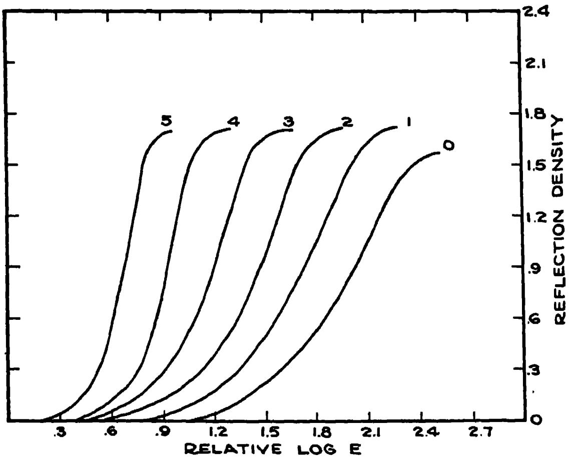

FIG. 257. Characteristic curves of Velox papers.

In practice, the development of negatives is carried to a fixed extent, which means that, if the scenes vary appreciably in brightness scale, the resultant negatives have a rather wide variation in density scale. To print these various negatives satisfactorily, different contrast grades of printing paper must be used. In Figure 257 are shown the characteristic curves[13] for six grades of a developing-out paper (Velox *F* Glossy). It is seen that they have approximately the same D_{max} value. The available exposure scale, however, varies from approximately 1.5 in log *E* units for the No. 0 grade to approximately 0.5 for the No. 5 grade. These materials, as well as practically all commercially available developing-out papers of the chloride type, are characterized by rather long sweeping toes, straight-line portions which, if existent, are very short (with respect to exposure scale), and shoulders which break rather sharply at relatively high densities and become parallel to the log *E* axis. It is interesting to see the shape of the negative *D*, log *E* curve required to fulfill the mirror image law and give perfect objective tone reproduction if the entire positive curve, from $D = 0$ to $D = D_{max}$, is to be utilized. The negative characteristics fitting the six positive materials in Figure 257 are shown in Figure 258. Negative materials having such characteristics are not available. But, as a rule, minimum densities less than 0.05 and maximum densities greater than 1.55 are not required in

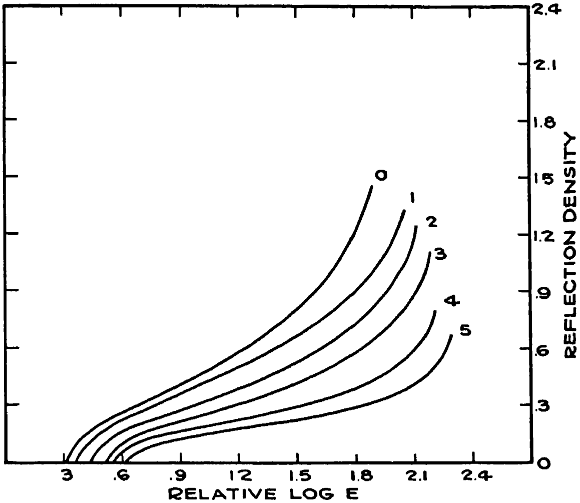

FIG. 258. Characteristics of negative materials fitting the characteristics of Velox papers.

positives. In Figure 259 are shown the positive characteristics so limited, and in Figure 260 are shown the negative characteristics giving a perfect fit.

The maximum density obtainable on developing-out papers[14] depends upon their surface characteristics. For surfaces having high gloss, 1.7 represents the approximate limit obtainable, although a few materials having somewhat greater values are available. If the surface is of a semimatte or velvet type, the D_{max} falls to approximately 1.55; while for dull, dead matte surfaces, the maximum obtainable density is not much greater than 1.30. It is obvious from this that there are many brightness scales in natural objects which cannot be reproduced by these materials. The average brightness scale of the one hundred and twenty-six exterior scenes previously discussed was 160, log BS_o = 2.2. Even for the average, therefore, some compression of brightness scale must be accepted. The maximum brightness scale of the same group was 760, log BS_o = 2.9, which is beyond the range of any photographic material coated on paper.

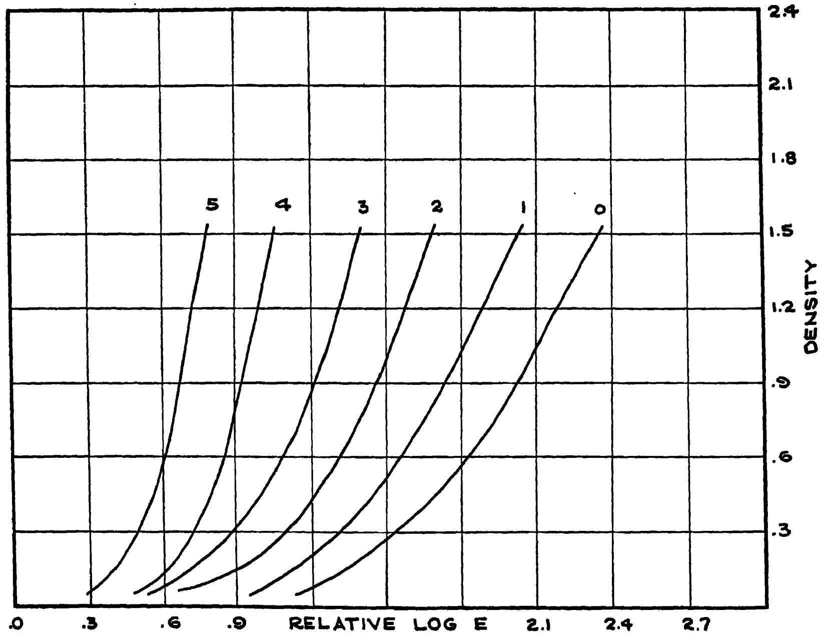

FIG. 259. Limited characteristics of positive materials.

Positive materials are also coated on a transparent support, such as lantern slide plates and motion-picture positive film. The exposure and density scales of these materials differ markedly from those of photographic papers, as shown by Figure 217 on page 706, which shows a family of curves for motion-picture positive film, the four curves resulting from different extents of development. The exposure scale decreases somewhat as the extent of development is increased. In the case of the shortest development time, $\gamma = 1.02$, for instance, this material could easily render a negative having a density scale of 2.2. Under these conditions, however, the density scale of the positive would be only about 2.2. For the longer times of development, the available exposure scale contracts to about 1.4, accompanied by an increase in the density scale of the positive, to approximately 3.5 With this material, therefore, it is possible to reproduce an object-brightness scale of over 1000 though in practice the full density scale is not used.

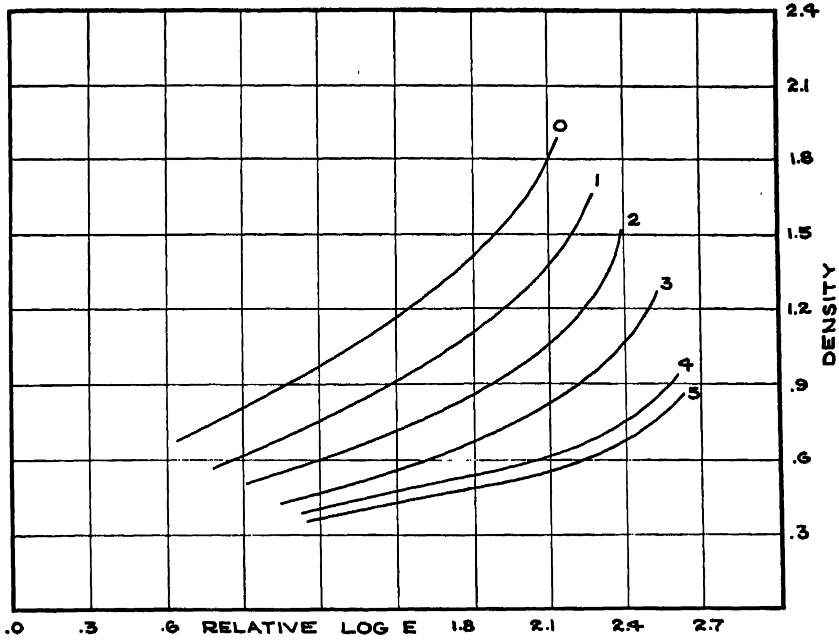

FIG. 260. Negative characteristics giving a perfect fit on the limited positive characteristics.

The development of motion-picture positive film processed in the large motion-picture laboratories is remarkably constant, and the result obtained from this highly standardized processing is shown in Figure 261. Examination[15] of a large number of samples from release prints indicated that the minimum density is, on the average, approximately 0.3, while maximum density is about 1.8. It is evident, therefore, that the entire available density scale of this product is not utilized. There are very definite reasons for not attempting to utilize the entire available density scale, as will be seen when the characteristics of reproductions are considered.

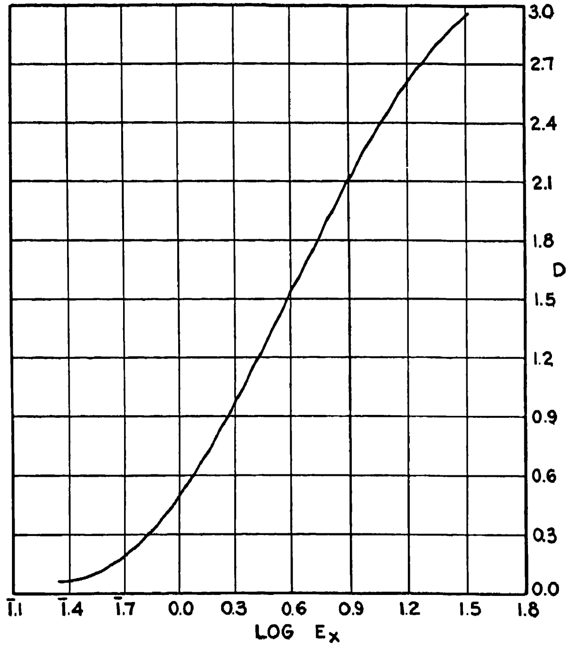

FIG. 261. Characteristic curve of motion-picture positive film with standard processing.

CHARACTERISTICS OF THE OBJECTIVE REPRODUCTION

A positive does not become the final objective reproduction until it is illuminated, and its final brightness characteristics depend upon this illumination. The illumination levels by which prints on paper are viewed are quite diverse. At night, the viewing light is wholly from artificial sources, and the illumination values may be as low as 5 and seldom exceed 20 foot-candles. Exhibition prints, of course, are usually hung on the walls for viewing. It seems reasonable to assume that the illumination levels vary from 10 to approximately 50 foot-candles. During daylight hours, illuminations from 200 to 500 foot-candles may be found near windows, while at points farther removed from windows these levels probably drop to 50 to 100 foot-candles. Prints are probably viewed out-of-doors to a relatively small extent, but the illumination would seldom exceed 1000 or perhaps 1500 foot-candles.

The reflectance values of prints may be 2 per cent for the lowest reflectance and 80 per cent for the highest. In Table LXXIX are shown the brightness values for some selected situations. It is seen that for prints viewed in interiors minimum brightnesses vary from 0.2 to approximately 4.0 foot-lamberts and the maximum brightness from 8 to 160 foot-lamberts. These brightnesses may be compared with those encountered in exterior scenes shown in the lower part of the table for high, average, and low illumination levels. It is evident from these data that the absolute brightnesses of exterior scenes are very seldom reproduced in the photograph. Fortunately, the reproduction of the absolute brightness values is of secondary importance because, as a study of the subjective phase of the problem shows, the sensation produced by a given stimulus (brightness) depends

TABLE LXXIX

Brightness of Prints

Location	I_p	B_p *min*	B_p *max*
Interior, night, average home	10	0.2	8.0
Interior, night, salons	20	0.4	16.0
Interior, day, near windows	200	4.0	160.0
Interior, day, away from windows	50	1.0	40.0
Exterior in shade	1000	20.0	800.0

Brightness of Scenes

	B_o *min*	B_o *max*
Exterior Low	1.0	200
Exterior Average	15.0	2400
Exterior High	50.0	10000
Interior Low	0.1	30
Interior Average	1.0	300
Interior High	4.0	1000

upon the condition of the observer's eye. A brightness of 1 or 2 foot-lamberts viewed with the eye adapted to a low level of illumination may produce a sensation resembling very closely that produced by a brightness of several hundred foot-lamberts when the eye is adapted to a higher level of illumination.

For positives projected onto a screen, as in motion-picture practice, the characteristics depend upon the projecting optical system and, especially, upon the flare light due to scatter from various parts of the equipment. For a thorough understanding of this situation, the entire theater must be considered as a piece of optical apparatus, because a considerable amount of light may reach the projection screen by reflection and from the room lighting. In Figure 262[16] is shown the effect of lens flare upon the characteristics of the screen image. The curve *A* represents the *D*, log *E* characteristic curve for motion-picture positive film and is similar to that in Figure 261. A positive of relatively low average density projected by a lens having appreciable flare appears to have the characteristic shown by curve *B*. There is no difficulty in rendering in positive film a density range of 2.5,

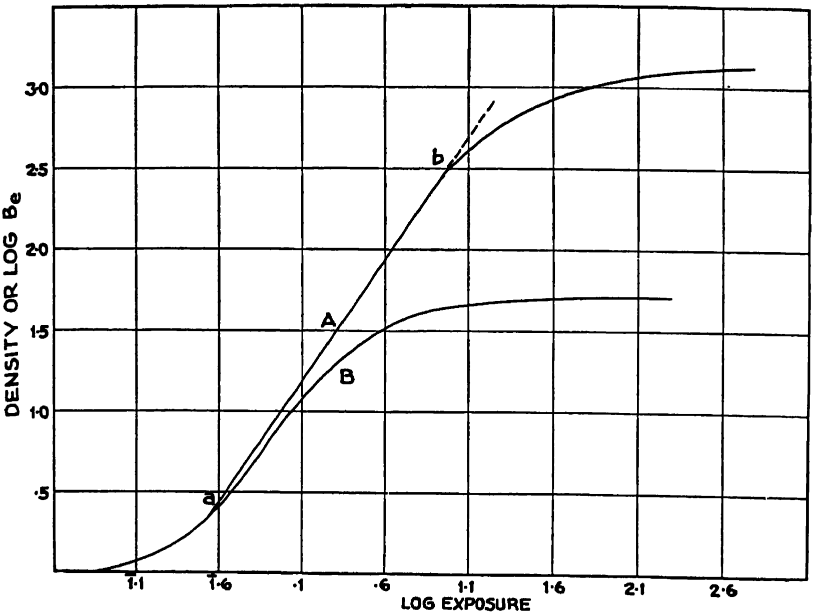

FIG. 262. Effect of lens flare upon the screen image.

which, of course, should give an image-brightness scale on the screen of 320. Owing to the effects of lens flare, however, the brightness scale illustrated in Figure 262 is only 50. The case is probably an extreme one, and for positives of higher average density and a modern lens system of high quality the flare due to the lens itself is appreciably less. Tuttle showed, in fact, that with a commercially available projection lens, such as is used extensively in motion-picture theaters, the degradation of projected image-brightness scale is very small. However, to this must be added the degradation of image contrast by general theater auditorium lighting. In a large theater of modern design, the scattered light from the auditorium illumination and the reflected light from such objects as walls, ceiling, and audience may easily amount to 0.1 to 0.4 foot-candles. In a projected image of which the maximum illumination is 15 foot-candles (a relatively high value) and the minimum illumination 0.15 foot-candle, the brightness scale of the image is reduced from 100 to 60, assuming an illumination from house sources of 0.1 foot-candle. It seems reasonable to assume that in motion-picture theaters, on the average, the brightness scale of the image falls between 40 and 70, depending upon specific conditions.

THE REPRODUCTION CURVE

The final step in the completion of the objective tone-reproduction cycle involves a comparison of the brightness characteristics of the reproduction with those of the original, as shown in the first quadrant of the tone-reproduction diagram, Figure 243. The general results may be illustrated by one or two typical examples. In the lower part of Figure 263 is shown a reproduction curve for an actual case. This represents the characteristics of the print[27] shown in the upper part of the figure. While it may be impossible to judge precisely from the half-tone reproduction, an inspection of this print by about two hundred observers led to the conclusion that its quality was equal to the best that could be made by any adjustment of negative exposure time and choice of printing paper contrast. In the lower part of Figure 264 is shown a reproduction curve for the photograph in the upper part of the figure, and this print in the opinion of the two hundred observers was very definitely of lower

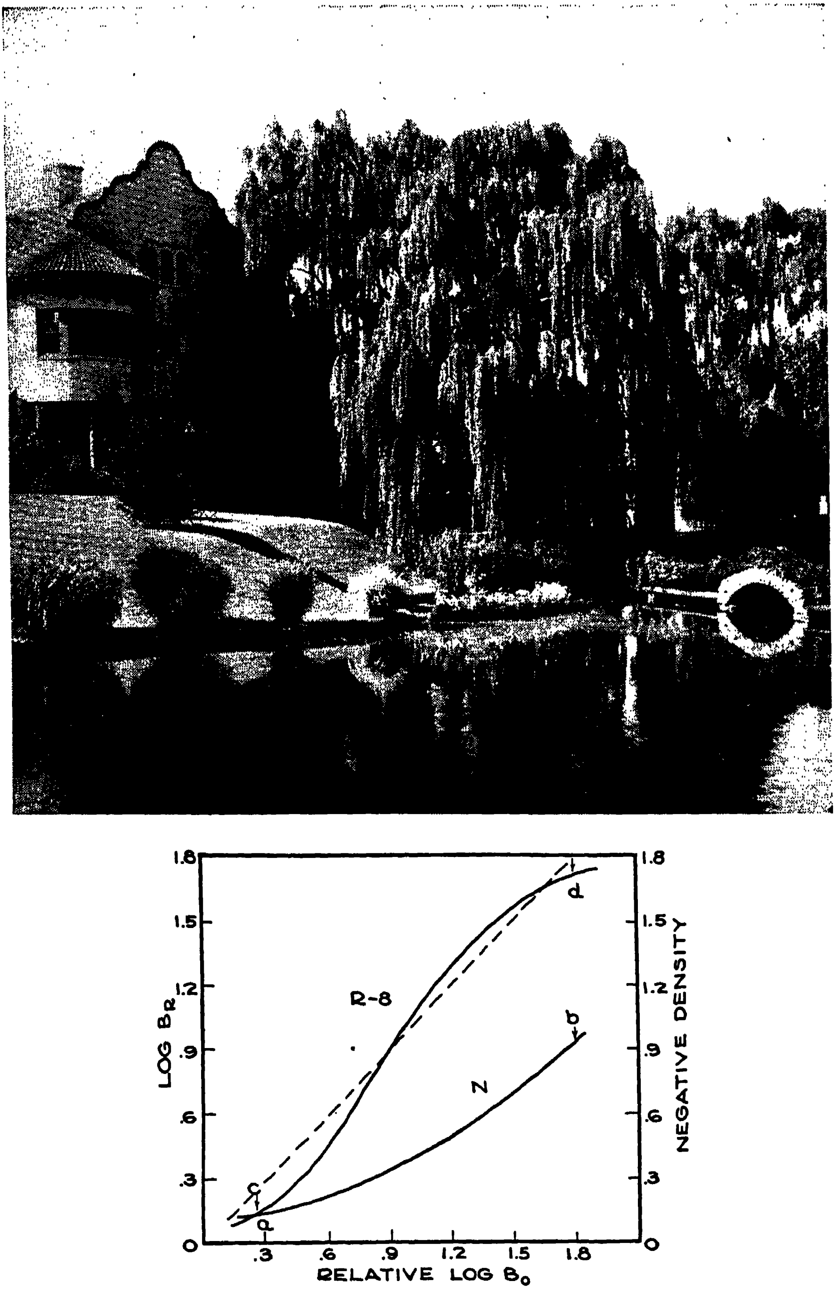

FIG. 263. Print and reproduction curve showing excellent quality.

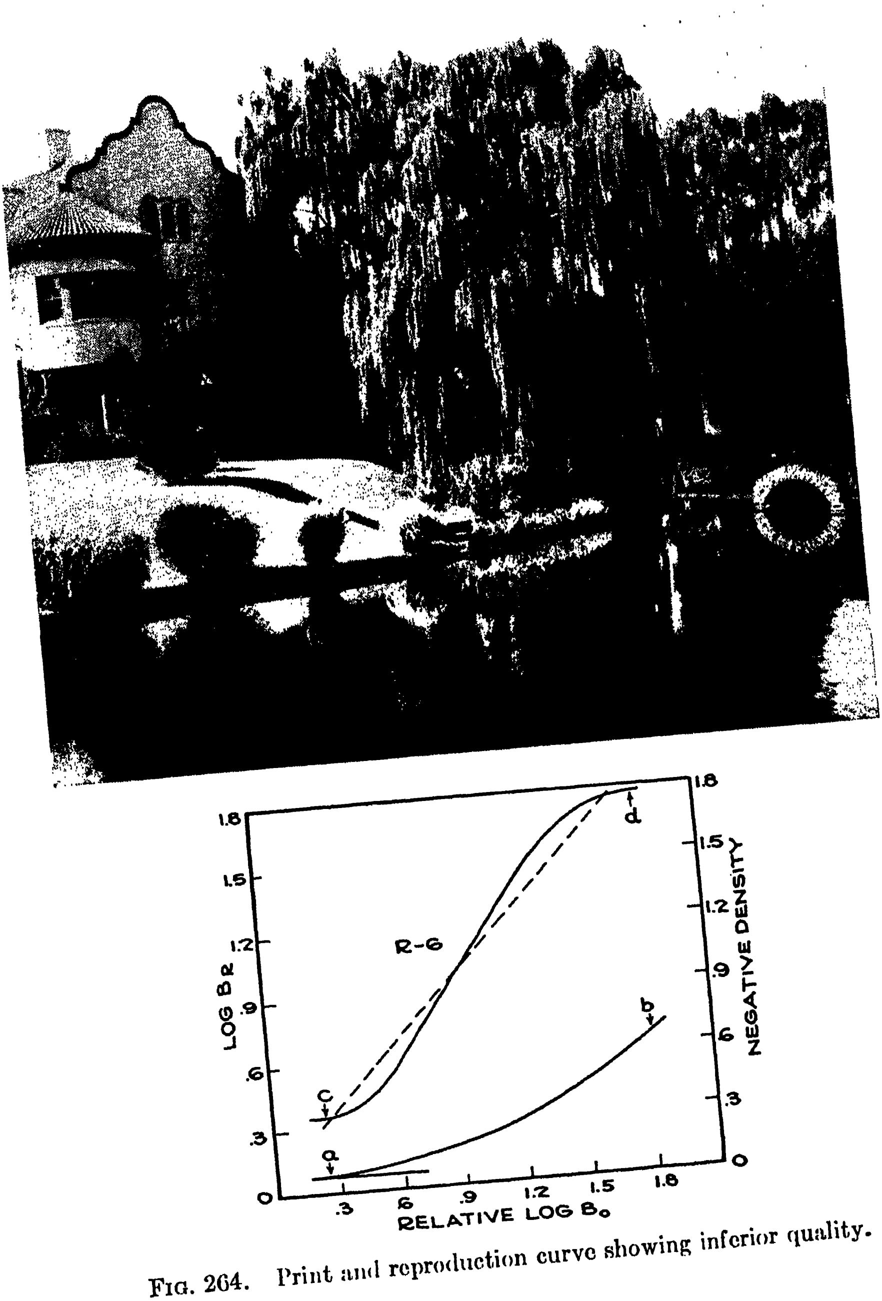

FIG. 264. Print and reproduction curve showing inferior quality.

photographic quality. Comparison of the reproduction curve in Figure 264 with that in Figure 263 indicates very clearly the significance of these curve shapes as indices of print quality. As plotted, the relative log B_o scale refers to the actual image brightness incident on the camera when the negative was made. The camera lens combination had in that environment a flare factor of approximately 2.0. Therefore, if the reproduction curve R-8 in Figure 263 were plotted against actual object brightnesses, it would appear as shown in Figure 265. It is seen that in this print a compression of approximately 50 per cent has been made in the brightness scale of the print compared to that of the object. However, since the curve R-8 deviates but little from a straight line, the compression is almost perfectly proportional although, of course, there is a little enhanced compression of the brightness differences in the extreme shadows and highlights and some expansion of the brightness differences in the middle tones.

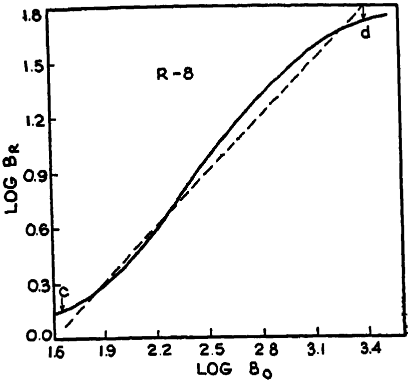

FIG. 265. Reproduction curve plotted against actual object brightnesses.

THE SUBJECTIVE PHASE

The purpose in making a photograph is generally to produce a representation which recreates in the mind of the observer the impressions received when the original was viewed. Consequently, the complete solution of the tone-reproduction problem involves a consideration of the subjective phase of the problem, expressed in the steps I and X of Figure 240, page 756.

The characteristics of the object and the image which are important in the objective phase of tone reproduction are those of *brightness* and brightness scale. While the same term is often applied to visual sensation, it tends to introduce confusion; and for the subjective phase the psychological correlative of brightness, *brilliance*, is preferable.

While sensation cannot be measured, strictly speaking, it can be evaluated in relative terms. For the solution of the tone-reproduction problem, the relationships of immediate importance are those which specify the sensitivity of the human eye to brightness differences. Weber[17] was probably the first to establish a relation between the brilliance characteristics of sensation and the stimulus. His work indicated that just noticeable brilliance differences at various levels were produced by a fixed ratio between the values of brightness. Fechner[18] expanded this into the so-called *Weber-Fechner law*, which, expressed in his own words, is that "as the stimulus grows in geometrical progression, the visual sensation resulting from the former grows in arithmetic progression." Expressed symbolically, this takes the form

$$\Delta S = K \cdot \frac{\Delta B}{B},$$

in which ΔS indicates a just noticeable change in the sensation and ΔB is a brightness increment which must be added to the brightness, B, for $B + \Delta B$ to appear noticeably different from B.

Many investigators have studied this law experimentally, and it appears that the relationship is valid over only a relatively short range of brightnesses. In Figure 266[19] are shown the experimental results obtained by different workers from 1865 to 1915.[20] It is seen that, in general, the agreement is good. $\frac{\Delta B}{B}$ is given as a function of log B and, therefore, expresses the retinal sensitivity to brightness differences in the inverse form, since the smaller the value of $\frac{\Delta B}{B}$, the greater the sensitivity to brightness differences. $\frac{\Delta B}{B}$ is seen to be approximately constant in the region from 1 to 250 foot-lamberts * but increases very much at brightness levels below 1 foot-lambert and begins to increase somewhat at brightness levels above 250 foot-lamberts.

These measurements were made with monocular instruments having artificial pupils so that there was no change of pupillary diameter for different illumination levels. Because of these limitations, the results shown in Figure 266 are not directly appli-

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* 1 foot-lambert is equivalent to 1.076 millilamberts.

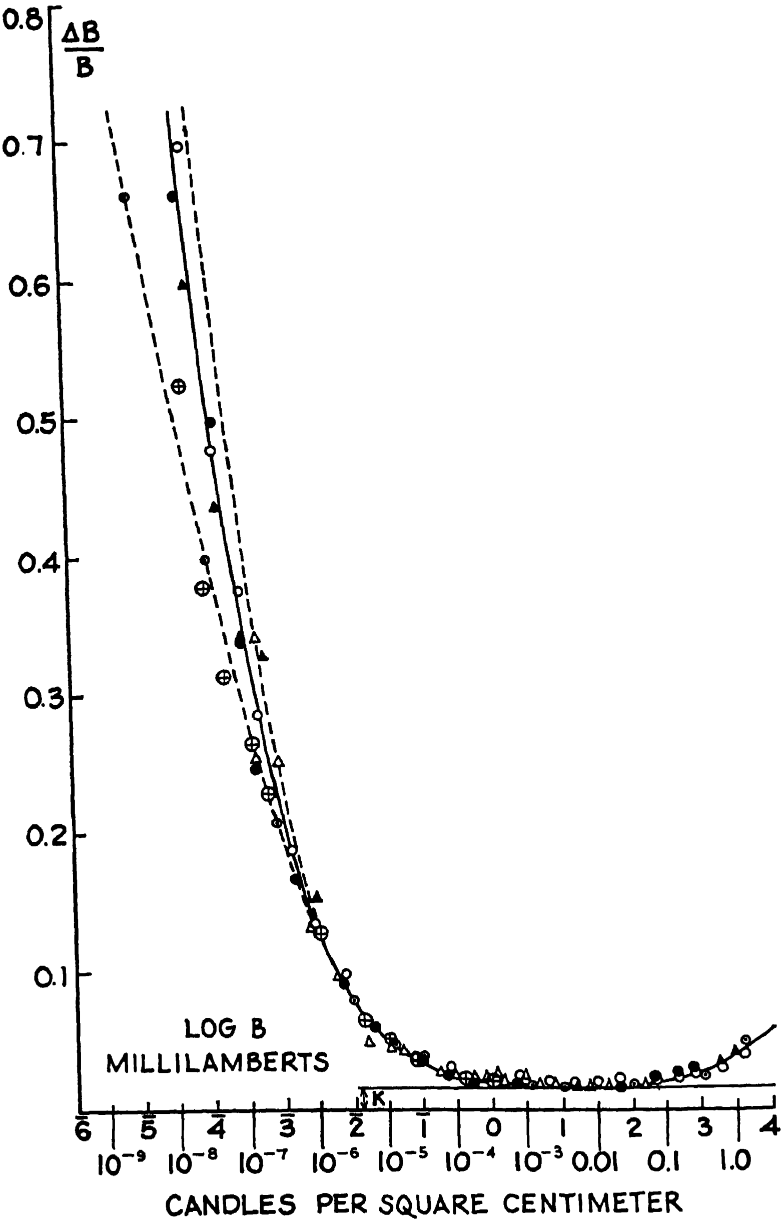

FIG. 266. Curve showing relation of retinal sensitivity to brightness.

cable to tone-reproduction problems. This can be illustrated by following the experimental methods used. Most of the visual field of the observer is filled with a surface illuminated to a brightness *B*. In the center, at a point on which the observer's attention is fixed, is a relatively small spot, usually subtending about 3 degrees at the eye of the observer, of which the brightness can be controlled. The observer adjusts the brightness of this spot until it is just noticeably more brilliant than the surrounding field. The difference between them is ΔB. The brightness of the peripheral field is then changed and the operation repeated until the entire range from the absolute threshold to the limit of the instrument has been covered. This procedure is not at all similar to the visual operations of an observer viewing a field under normal conditions. Then the field consists of a heterogeneous mosaic of areas differing in brightness, and the eye is called upon to differentiate brightness differences in this field. While there is usually a considerable difference between the highest and lowest brightness in such a scene, it is much smaller than that shown in Figure 266, which extends from 0.0001 foot-lambert to 5000 foot-lamberts and covers a brightness scale of 50,000,000. The average brightness scale in exterior scenes is approximately 160 and the possible maximum value of the order of 1000. As the attention of the observer of a scene wanders from point to point, there is probably some change in retinal sensitivity owing to variations in the illumination; but, in general, the sensitivity of the retina is stabilized by the average brightness of the scene and the peripheral surroundings. The information, therefore, required for the solution of tone-reproduction problems relates to the sensitivity of the eye to brightness differences when the general sensitivity of the eye is stabilized. Lowry[21] attacked this problem and published results for a relatively few conditions in the region of medium and low brightnesses. His method is described below.

The visual sensitometer consists of a hemisphere having a radius of one meter, the interior surface of which is covered with a matte white paint. Observations are made from approximately the center of this hemisphere. In this way, the entire visual field is of uniform brightness, the value of which can be adjusted from 0.0005 foot-lambert to approximately 600 foot-lamberts. At the pole of the hemisphere is located a test field, circular in shape, which subtends an angle of approximately 2.5° at the eyes of the observer. The test field consists of two parts, the division being along its vertical diameter; and the brightness of each part can be adjusted independently from 0 to a fairly high level. The appearance of the visual field is illustrated in Figure 267. The large circle indicates the outer boundary of the hemisphere, which forms the *sensitizing field.* The brightness of this is designated as B_f. The small circle at the center represents the *test field,* the two parts of which are designated as x and y, and the brightnesses of these test fields at any time are B_x and B_y. This test field is viewed with both eyes without any obstruction between the eyes and the test field.

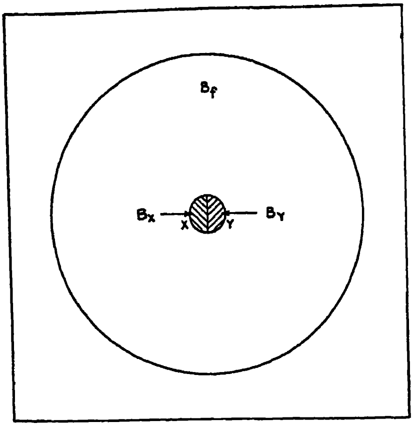

FIG. 267. Field of visual sensitometer.

To determine a *specific* contrast sensitivity, the field brightness, B_f, is set at some value for which it is desired to determine the specific contrast sensitivity. The first step is to determine the brightness of subjective black, and this brightness is that which produces a brilliance of 0. The brightness of one part of the test field, for instance, y, is set at a very low value. The brightness of x is then set to be just noticeably less brilliant than y; then the brightness of y is reduced so that the brilliance is just noticeably less than that of x. This is continued until a further reduction in the brightness of y by any amount does not produce a lesser brilliance than that of x. The brightness of the x part of the field is that of subjective black (brilliance = 0) for this condition. A similar process is then followed, but in the reverse order; in fact, two general techniques may be used: one known as the *step-by-step method* and the other, the *discontinuous method.* In the former, assuming that the x part of the test field is set at subjective black, the brightness of y is raised until it is just noticeably more brilliant than x; and from the calibrated scales of the instrument the value of ΔB ($\Delta B = B_y - B_x$) is recorded. ΔB corresponds to a *just noticeable* brilliance *difference* (j.n.d.) and is the fundamental unit in which sensation is evaluated. The brightness of x is raised until it is just noticeably more brilliant than y, and again the value of ΔB is determined. This is continued until the upper limit of the instrument is reached. From the values of ΔB plotted along the abscissa axis, adding one unit to the ordinate values for each step, the response curve of the eye for this particular condition of adaptation can be determined directly.

The procedure described above is extremely laborious, and usually the discontinuous method is used. This involves the setting of one part of the test field, y, for instance, to some known brightness value and then adjusting the other part, x, so that there is a just noticeable brilliance difference between the two halves of the field. The brightness of y is changed by a suitable amount and the process repeated. In this way, values of ΔB and B are determined, and the ratio, either $\frac{\Delta B}{B}$ or $\frac{B}{\Delta B}$, can be plotted as a function of B. This procedure does not give the response curve directly but yields the first derivative of the response curve if $\frac{B}{\Delta B}$ is plotted.

In Figure 268, plotted from Lowry's data, are shown two contrast sensitivity curves: A, for a sensitizing field brightness, B_f, of 10 foot-lamberts and B, for 93 foot-lamberts. The values of $\frac{\Delta B}{B}$ are plotted as ordinates. These ordinates are, of course, inversely proportional to the contrast sensitivity of the eye. It is interesting to note that in the curve for $B_f = 10$ foot-lamberts, the maximum sensitivity occurs where B has a value of 10 foot-lamberts and that in the curve for $B_f = 93$ foot-lamberts, the maximum sensitivity occurs at a B value of approximately 93 foot-lamberts. This, of course, is to be expected, since when one part of the test field x has a brightness equal to B_f, the experimental conditions are similar to those used in the determination of the general sensitivity relationship shown in Figure 266. Thus, for any specific brightness contrast function, the maximum sensitivity occurs when the test field matches the brightness of the peripheral or sensitizing field. This is in accordance with the findings of Cobb[22] and Dittmers.[23] This condition can hold over only a restricted brightness range, however, for, as shown by Lowry's data, when B_f is low (0.0005 foot-lambert, for instance) the maximum sensitivity is not at B_x or $B_y = 0.0005$, but at 10 foot-lamberts.

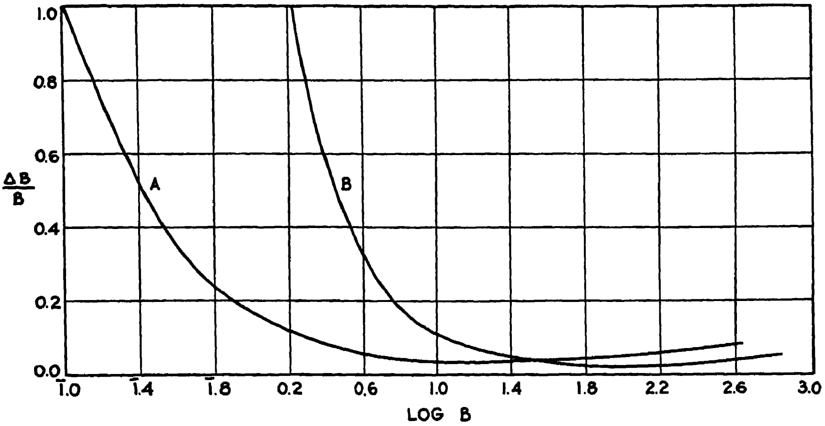

FIG. 268. Contrast sensitivity curves for two levels of field brightness.

In Figure 269, the data contained in the B curve of Figure 268 are replotted as curve A, using $\frac{B}{\Delta B}$ as ordinates. These ordinates are now directly proportional to sensitivity, and by integration of the curve the response curve B is obtained. While it may be possible to write an analytical expression representing curve A and then to derive curve B by integration, it is simpler to rely upon graphic integration for the determination of curve B. The ordinates are, of course, in arbitrary units depending upon the integration constants. But it is quite possible to convert these ordinates into the fundamental sensation unit, a just noticeable difference. In the particular case illustrated in Figure 269, this conversion can be made by dividing the ordinate values by 0.44. The vertical dotted line, OM, is drawn where B_f is equal to 93 ft.-l., the brightness of the sensitizing field. The ordinate of the response curve at this point, 30.2, divided by the integration constant gives 68; and this is the number of steps of just noticeable difference between subjective black and the sensitizing field brightness, 93 foot-lamberts. Curve *B* represents for the eye under these particular conditions a function directly analogous to the *D*, log *E* relationship for a photographic material,

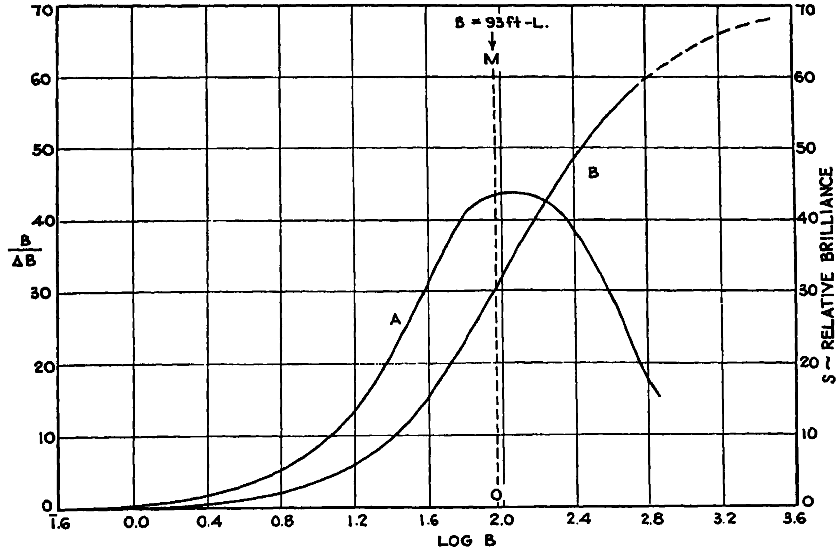

FIG. 269. Sensitivity brightness curve with high level of sensitizing field.

and it is interesting to note that this curve proves the fallacy of many statements concerning the relative response characteristics of photographic materials and the human eye. The eye is frequently stated to operate over an enormous range of brightnesses, such as 1 to 100,000,000, while the photographic plate has a relatively restricted exposure latitude, of the order of 1000 or possibly 2000. The impression given by such a statement is misleading, because curve *A* in Figure 269 shows that the ability of the eye to discriminate between brightness differences in a particular visual field is relatively restricted. For instance, the sensitivity of the eye to brightness differences has a low value at log $B = 0.8$. From this, it rises and passes through a maximum at log $B = 2.0$ and then decreases. Unfortunately, the experimental determinations have not been carried into a very high brightness region, but an extrapolation of the curve indicates that it does not extend far beyond log $B = 3.0$. The range is therefore 2.2 in log units, corresponding to a brightness scale of 160. This is less than the exposure latitude of a high-quality negative material.

In Figure 270 are shown a pair of curves analogous to those shown in Figure 269, but they apply to a sensitizing field brightness, B_f, of 10 foot-lamberts. Unfortunately, the curves in these two figures are not exactly comparable since they are derived from observations by two different groups of observers, but they serve to illustrate a point of interest. If the value of the sensitizing field is decreased sufficiently, the contrast sensitivity must also decrease, as indicated by the general law, Figure 266. If the data embodied in the curves in Figure 270 are accepted at their face value, it will be evident that at this adaptation level, 10 foot-lamberts, the sensitivity to brightness differences is lower than in the case of B_f = 93 foot-lamberts (Figure 269). The graphic integration constant is the same in the response curve in Figure 269, and the number of just noticeable differences can again be determined by dividing the ordinate numbers by 0.44. In this case, therefore, the number of just noticeable steps between subjective black and the sensitizing field brightness is 54 compared with 68 for the higher level.

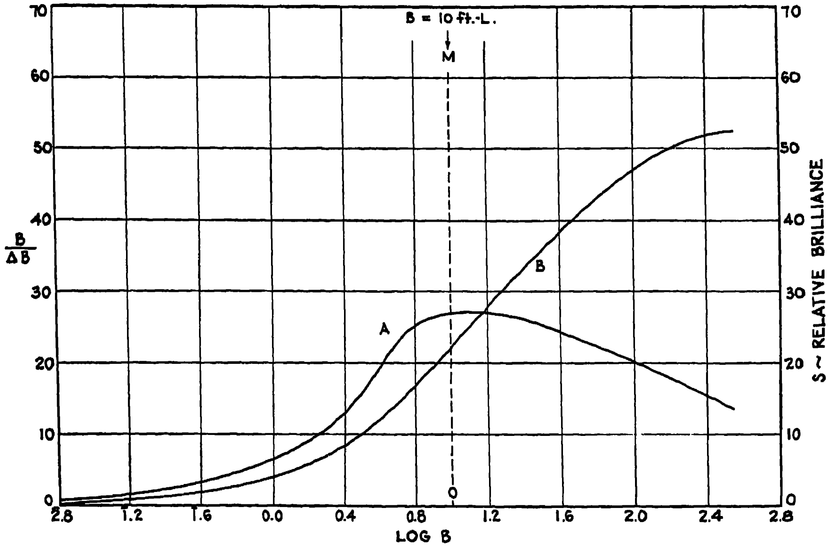

FIG. 270. Sensitivity brightness curve with low level of sensitizing field.

The propriety of adopting the just noticeable difference as a measuring unit for sensation has been discussed at length, but no definite decision has been reached. Troland[24] points out that in attempts to measure sensory differences *any arbitrary difference* might be selected as a suitable sensation unit. It is then necessary to find a method of determining when two such arbitrary differences are equal. The most logical suggestion is that the two differences should *appear* equal, but this criterion is difficult to apply. Troland states:

> "With these considerations in mind, we may feel well justified in choosing, as our unit in psychical measurement, that degree of difference between the elementary qualities in any scale or series which can be most readily established and reproduced. The quantity which fulfills this requirement appears to be what is called the *differential threshold* or the 'just noticeable difference' (j.n.d.). This is the minimum difference detectable in any region of a given series of qualities."

From a consideration of the specific contrast sensitivity data illustrated in Figures 269 and 270, it is evident that the available information is inadequate for satisfactory treatment of the subjective aspects of tone reproduction. Aside from the values published by Lowry, there is little information in the literature. Abribat[19] studied the problem in considerable detail. He followed the general method of Lowry, but his test field was very much more complicated. Instead of the eye seeing a simple two-part photometric field in the center of the sensitizing field, it is confronted with a rather complex test object comprising a large number of different brightnesses and contrasts. Abribat argues, and perhaps correctly, that the data should be obtained under conditions approximating as closely as possible those occurring in practice. He published specific contrast functions for sensitizing field brightnesses of 0.00047, 11 7, 58, and 117 foot-lamberts. As in Lowry's work, no information is given for higher sensitizing field brightnesses. In exterior scenes, average brightnesses may reach 5000 or even 10,000 foot-lamberts. Further data are therefore needed in this field. Abribat applied his results to the prediction of tone-reproduction results using diagrams similar to those presented here.

The application of the specific contrast sensitivity data illustrated in Figures 269 and 270 is given in Figure 271 for a particular case. On the abscissa is a logarithmic scale on which the object brightness of a hypothetical scene having an average brightness of 400 foot-lamberts may be located. On the average, the maximum brightness is approximately four times the average brightness, while the brightness scale of an average scene is 160 (log BS_o = 2.20). The minimum brightness of this scene, therefore, falls at log B_o = 1.0, and the maximum brightness, at log B_o = 3.2. The visual response curve for an average field brightness of 400 foot-lamberts is drawn as indicated. This is extrapolated from Lowry's data and is placed on the log B_o axis so that the curve starts from log B_o = 0.0, which is the brightness of subjective black as determined for these conditions. If a series of points are selected on the log B_o scale, perpendiculars are drawn to cut the visual response curve, and horizontal lines

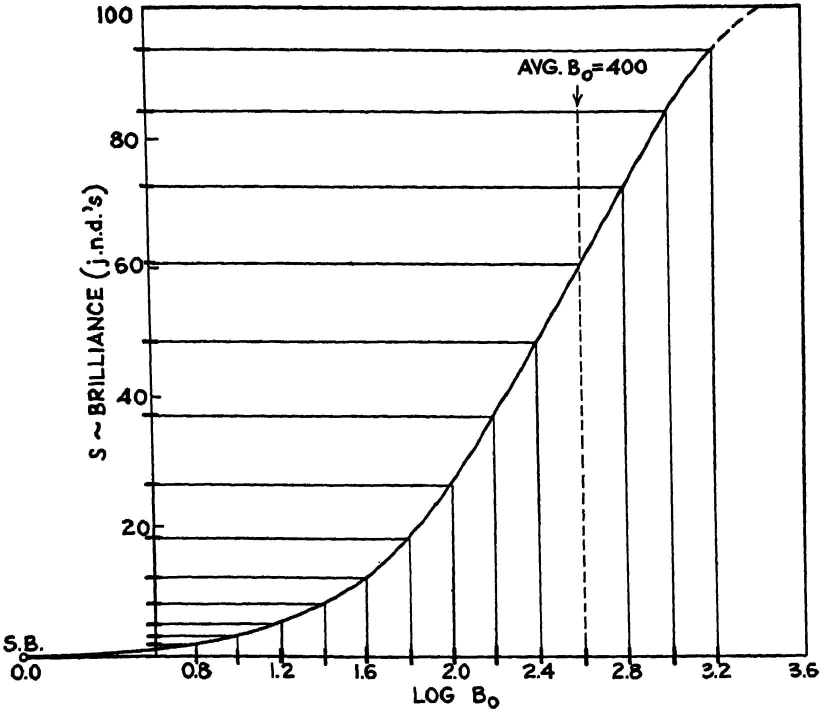

Fig. 271. Application of the response curve to a definite brightness scale.

through the points thus located are drawn to cut the brilliance scale at the left, the spacing of the points thus determined will indicate the magnitude of the brilliance intervals corresponding to a fixed ΔB_o; namely, $\Delta \log B_o = 0.20$. It is seen that a considerable portion of the brightness scale is covered by the straight-line portion of the response curve, and in this region a fixed logarithmic increment in B_o produces a constant increment in brilliance. In the region of low object brightness, however, the curve is not straight, and the relative brilliance intervals are therefore less than those occurring in the higher brightness range. Thus, there is a compression of shadow detail due to the visual characteristic.

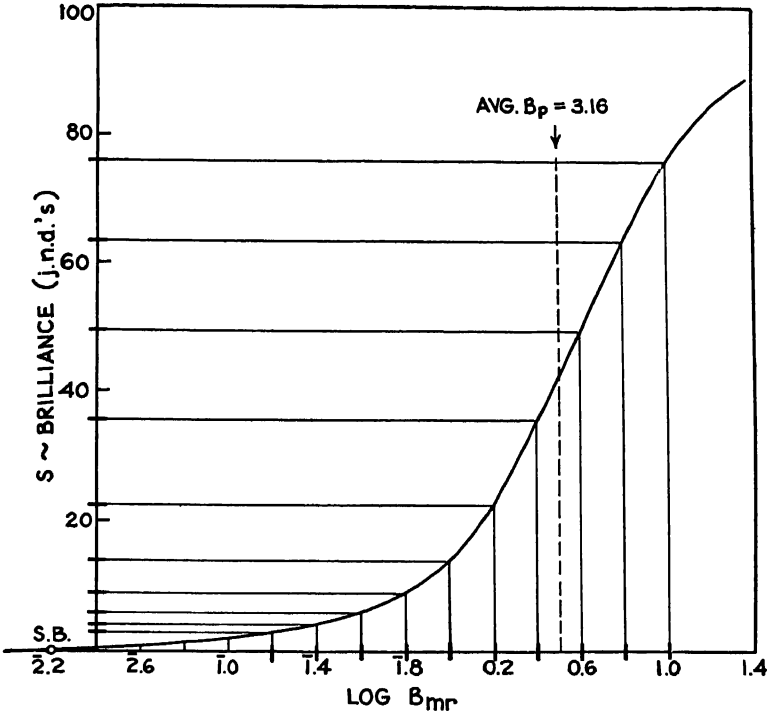

FIG. 272. Application of the response curve to a photographic reproduction.

The same procedure can be applied to the determination of the brilliance response when viewing the photographic reproduction, and this is illustrated in Figure 272. The sample print is assumed to have a minimum brightness of 0.25 foot-lambert and a maximum brightness of 10 foot-lamberts and to be viewed with an illumination of 12 foot-lamberts, which corresponds approximately to artificial illumination in an average home. The manner of drawing the response curve is similar to that used for Figure 271. Under these conditions, subjective black falls at $\log B = -2.2$, which is considerably below the minimum brightness of this print under these conditions. On the relative brilliance scale at the left is seen the rendition of points equally spaced on the $\log B_{mr}$ scale, and the considerable and differential compression will be evident. A comparison of the grouping of points on the brilliance scale in Figure 271 with those in Figure 272 gives a direct measure of the similarity between the brilliance characteristics of the scene as viewed by the observer and those of the print as viewed under artificial illumination.

This comparison is most conveniently made by using a tone-reproduction diagram such as that in Figure 273. In quadrant III is the usual objective tone-reproduction curve taken from the upper right-hand quadrant of the objective tone-reproduction diagram shown in Figure 243. On the line NM is established a scale of $\log B_o$. On this scale are located points corresponding to various object brightnesses. A scene having a brightness scale of 160 is assumed, the average brightness being 400 foot-lamberts and the maximum brightness four times the average; that is, 1600 foot-lamberts. The $\log BS_o$ value is 2.2 between points a and l. On the line NP is established a scale of objective reproduction brightnesses. The letters a, b, c, to l, inclusive, indicate the brightness values in the objective reproduction of the reproduction areas corresponding to the similarly lettered areas of the object as shown on the $\log B_o$ scale. The objective reproduction has a maximum brightness of 10 foot-lamberts and a minimum of 0.25, giving a brightness scale of 40. This represents an average condition for a paper print viewed under illumination conditions frequently found in interiors at night. The reproduction curve, A, is of the form previously discussed.

To construct the subjective reproduction curve for convenient comparison with the objective reproduction curve, the scale of $\log B_o$ values must be transferred to the line MO; and this is done by rotation as indicated by the dotted circular segments having a common center at the point M. The chosen object areas are represented by a, b, c, to l on this new scale. Similarly, the log B_{mr} scale is transferred to the line OP as indicated by the circular segments having a common center at the point P. The object areas are now represented by the letters a, b, c, to l, inclusive. In quadrant IV is plotted the specific brightness con-

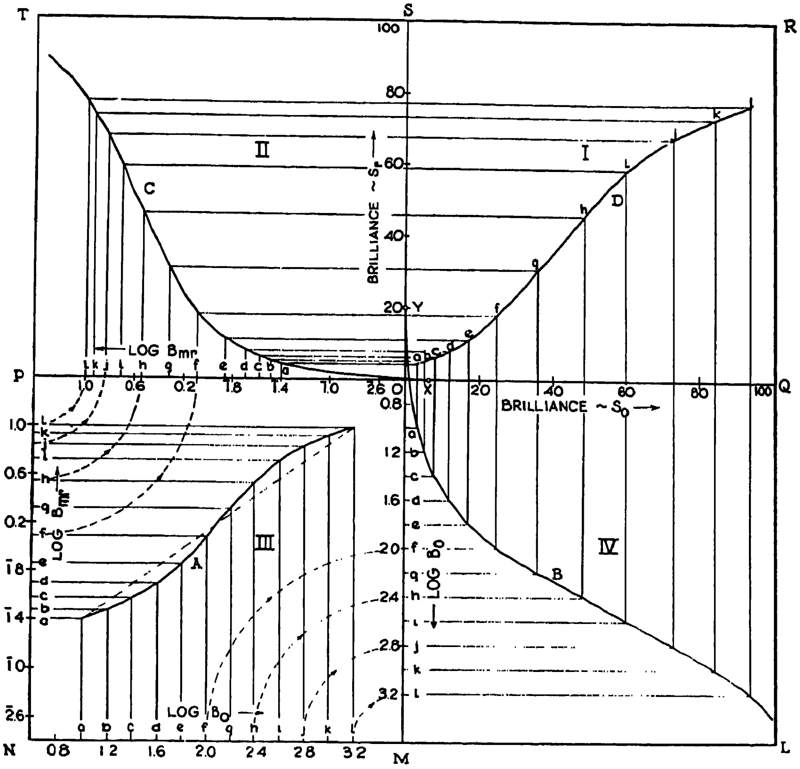

FIG. 273. Tone-reproduction diagram involving the subjective phase.

trast curve for the eye determined for an average field brightness of 400 foot-lamberts. This curve must start at subjective black, indicated by the point Y, having a log B_o value of 0.00. On the line OQ is established a brilliance scale, and the shape of curve B in quadrant IV is adjusted so that the brilliance values indicated represent the number of just noticeable brightness differences between subjective black and a particular point. Horizontals through the points a, b, c, to l, inclusive, on the OM axis intersect the curve B, and from these intersection points verticals establish the corresponding brilliance values on the scale OQ.

In a similar manner, the specific contrast function determined for an average field brightness of 3 foot-lamberts is plotted in quadrant II as curve C. Here, again, the curve must start from O brilliance at the brightness corresponding to subjective black, as indicated by the point x, which has a log B_{mr} value of -2.20. Verticals through the points a, b, c, to l, inclusive, on the OP axis intersect the curve C, and from these points the intersection horizontals establish on the brilliance scale on the axis OS the brilliance values of the subjective reproduction corresponding to the original chosen object-brightness values indicated on the axis MN. Horizontals through these points, intersecting the verticals through the points established on the OQ axis, determine the final subjective reproduction curve, D, in the quadrant I.

In the particular example chosen, the subjective factors produce relatively little distortion in the shape of the final subjective reproduction curve compared with the objective reproduction curve, A. While there is a definite compression of shadow detail when the observer looks at the original (as compared with fixed increments in ΔB_o), some compression of shadow detail occurs when the observer views the objective reproduction, and these two practically balance each other. This analysis indicates that subjective factors become important only when the brightness levels in the object and those in the reproduction differ from each other much more than in the case represented in Figure 273. Considering the illumination conditions under which photographic reproductions are viewed, it seems unlikely that in photographic reproductions of relatively bright scenes, subjective factors produce much distortion in appearance. In an extreme case, however, such as a photographic reproduction of a moonlight scene, in which the illumination is about 0.025 foot-candle, while the positive is viewed under normal illumination levels, these subjective factors may become of considerable importance. Under such conditions, the objective reproduction can be distorted so that its appearance is similar to the original viewed under specified illumination conditions.

Since the specific visual response curves, C and D, shown in Figure 273 are plotted in terms of the fundamental sensation unit (just noticeable difference), the following conclusion may be drawn as to the appearance of this hypothetical scene and its photographic reproduction: The lowest brightness in the scene, indicated by point *a*, is only three steps above subjective black, while the maximum brightness, point *l*, is 93 sensation units above subjective black, giving a brilliance scale of 90 j.n.d's. On the other hand, the lowest brightness in the photographic reproduction is four steps above subjective black, while the highest brightness is 73, giving a brilliance scale for the reproduction of 69 j.n.d's. The average slope of the subjective reproduction is the ratio of 69 to 90, or 0.76.

It is also possible to obtain some idea as to the brightness values in scene and reproduction which will produce the same brilliance values for the two accommodation levels illustrated in Figure 273. For instance, the object area, *f*, has a brightness of 100 foot-lamberts, which produces a brilliance of approximately 25 j.n.d's. above subjective black. The same brilliance value will be obtained if the photographic reproduction is viewed by a brightness lying between points *g* and *f* at a log B_{mr} value of 0.24, corresponding to an objective reproduction brightness of 1.74 foot-lamberts.

Thus far, it has been assumed that the average visual field brightness determines the sensitivity of the eye to brightness differences and also the brightness of subjective black. Some unpublished data obtained by Lowry indicate that this assumption is not strictly correct. A small portable visual sensitometer suitable for the measurement of the brightness of subjective black was constructed, and determinations of the brightness of subjective black were made by placing this instrument at various points of outdoor scenes. The results for a particular case may be of interest.

The integrated brightness of the scene was 1000 foot-lamberts; the maximum brightness, 3500 foot-lamberts; and the minimum, 15 foot-lamberts. On the assumption that the average field brightness determines the brightness of subjective black, this value should be 25 foot-lamberts irrespective of the point in the scene to which the observer's attention is directed. However, it was found that if the observer's attention were fixed for a few minutes on the region of lowest brightness, the brightness of subjective black was actually 7 foot-lamberts, appreciably less than that indicated by the average field brightness value. On the other hand, if the visual sensitometer were moved into the region of highest brightness, the brightness of subjective black was approximately 28 foot-lamberts, only slightly greater than the value corresponding to the average field brightness. Thus, in this particular scene, the value of subjective black changed from 7 to 28 foot-lamberts, depending upon the part of the scene on which the observer's attention was fixed.

These results indicate that a visual response curve, such as that shown in Figure 273, is not strictly applicable to the tone-reproduction problem for a scene in which the brightness varies over a considerable range from one area to another. It is obvious, however, that the average field brightness does exert a marked stabilizing influence upon the sensitivity of the eye. Otherwise, the brightness of subjective black, when attention was fixed on the lowest brightness in the scene mentioned above, 15 foot-lamberts, would have been 0.2 foot-lambert instead of 7.0. The specific contrast sensitivity curve, beginning at a subjective-black value of 7 foot-lamberts, is very similar in shape to that for a subjective-black value of 28 foot-lamberts but displaced slightly in position. A composite curve can be constructed from these two which will probably fit well the actual requirements of a response curve for use in the solution of tone-reproduction problems.

It should be emphasized that the specific visual response curves used in Figure 273 are derived from a relatively few readings by one individual. Before the subjective phase of this problem can be dealt with with greater certainty, a large mass of data must be accumulated from a large group of observers so that the average may be taken as representative of the average normal human eye. Moreover, there is a little uncertainty in curve *B* because it was extrapolated from readings made at considerably lower brightness levels.

THE QUALITY OF PRINTS

In his work on the determination of speeds of the negative materials in terms of print quality (Chapter XIX, p. 716), Jones[27] studied the specification for the quality of prints, using both statistical and sensitometric methods. For the statistical method, a print was made from each of twelve negatives on the same material, for which the negative exposures had been increased progressively from the first to the last in the series. Each print is the best that could be made from its negative on any of the available contrast grades of printing paper. Four negative materials were studied in this manner.

As the first step in the application of the statistical method, the observer was instructed to arrange the prints in each group in the order of ascending quality, from left to right. The positions are indicated arbitrarily by numbers from 1 to 12, 1 being assigned to the worst quality and 12 to the best. This judgment was made by thirty observers, twenty of whom made a second series of judgments after a sufficient lapse of time to avoid an accurate memory of their first judgments.

TABLE LXXX

ILLUSTRATION OF METHOD OF EVALUATING RELATIVE QUALITY JUDGMENTS

Score for Print No. 12			*Score for Print No. 11*		
No. of Times	*Position*	*Points*	*No. of Times*	*Position*	*Points*
8	12	96	9	12	108
13	11	143	13	11	143
12	10	120	3	10	30
13	9	117	7	9	63
2	8	16	17	8	136
2	7	14	1	7	7
Total 50		506	Total 50		487

Fifty judgments having been obtained on each of the four sets of prints, several methods were available for combining the values to give numbers indicative of relative quality. According to that adopted, if a given print were placed in position 12, a score of 12 points should be credited to that print, while if it were placed in position 8, a score of 8 points should be assigned. The scoring is illustrated in Table LXXX for prints No. 12 and No. 11 made on material C. The multiplication of the numbers in columns one and two gives those in the last column, and the total of the numbers in the last column is the score for each print; 506 for No. 12 and 487 for No. 11.

A summary of the score of the prints made from material *C* is shown in Table LXXXI. In the line designated as "Actual" are the total scores for each print. In the line below designated as "Normal" are the results that would have been obtained if the prints had been placed according to negative number. The first four prints received what may be called "normal scores," indicating that all observers agreed that quality increased with negative exposure. Print No. 5 obtained a score slightly above its normal value. The same is true of prints Nos. 6, 7, 8, 9, and 10, while 11 and 12 obtained scores below the normal value. The fact that the scores for prints 8 to 12, inclusive, are so nearly equal indicates that there is very little difference in the quality of the prints in this group according to the judgment of the group of observers. The differences of quality, in fact, are so small that the positions of the prints within the group are almost those of probability, which would, of course, result in identical scores for all prints. Adjusted values of relative print quality, shown in the last line of the table, were obtained by assuming the average score of prints 8 to 12, inclusive, to be 100 and adjusting all of the actual scores proportionately.

TABLE LXXXI

Summary of the Score of the Prints Made from Material *C*

	Print No.											
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*
Actual	50	100	150	200	272	305	393	479	481	477	487	506
Normal	50	100	150	200	250	300	350	400	450	500	550	600
Adjusted	10	21	31	41	56	63	81	98	99	98	100	104

The adjusted values are shown graphically in Figure 274. The small circles represent the plotted values, and the solid curve is drawn in its most probable position.

This scale of relative quality has neither absolute significance nor is it necessarily linear with reproduction quality. The fact that a straight line is obtained for the first four prints must not be interpreted to mean that the difference in reproduction quality between prints 1 and 2 is the same as that between 2 and 3 or 3 and 4. The line is straight simply because consecutive numbers were assigned to the positions of the prints in order of reproduction quality. It is possible to obtain direct experiential judgment of the magnitude of quality differences between adjacent prints. Such judgments, however, are made with difficulty, especially by observers unskilled in this type of psychophysical observation. However, some data of this type have been accumulated, but many more observations are needed to establish the *shape* of the reproduction quality-negative exposure curve with certainty.

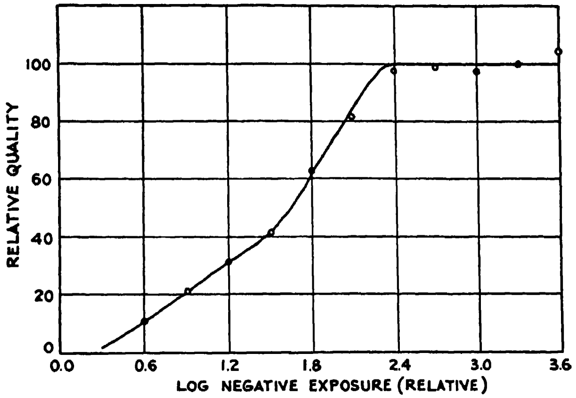

FIG. 274. Relation of print quality to negative exposure.

The determination of the relation between print quality and negative exposure by the statistical method, as described above, is a long and laborious process, and a means whereby the "quality" of a print may be computed from direct sensitometric measurements is desirable. An empirical formula for print quality can be based upon assumptions which seem reasonable in the light of tone-reproduction theory. These assumptions are that the satisfactory reproduction of brightness differences has a most significant bearing on the resultant print quality and that it should be possible to evaluate print quality largely in terms of the gradient errors found in the reproduction.

For the characteristic curve of a negative material, for instance, that in Figure 243, the density gradient, or slope G_n, at any point on the curve is given by

$$G_n = \frac{dD}{d \log E_x}.$$

Likewise, the density gradient, G_p, for the positive material is given by

$$G_p = \frac{dD_p'}{d \log E_y},$$

while the density gradient for the reproduction curve is given by

$$G_r = \frac{d \log B_{mr}}{d \log B_o}.$$

These three quantities for corresponding points, such as b_n, b_p, and b_x, are related by the expression

$$G_n \cdot G_p = G_r.$$

The gradient in the reproduction is equal to the product of the corresponding gradients of the negative and positive characteristics. If G_r is plotted against $\log B_o$, the curve is of the type shown in Figures 275 and 276. These show the gradient error curves for the best prints from negatives No. 4 and No. 8 of the experimental group. Perfect reproduction would be represented by the horizontal line shown at a gradient value of 1.0. In general, the gradient in the shadow region is too low (less than unity); while through a middle-tone region it is too high (greater than unity), decreasing to a value less than unity in the highlight region. The gradient error, ΔG, for any point a on the object-

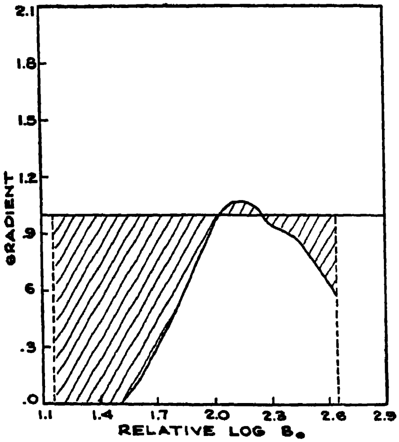

FIG. 275. Gradient error curve for print from negative No. 4.

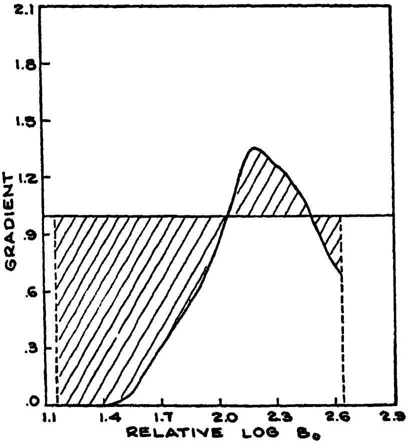

FIG. 276. Gradient error curve for print from negative No. 8.

brightness scale may be represented by $1 - G_a$. From a determination of the total area of the shaded regions (Figures 275 and 276) and its division by the logarithm of the object-brightness scale, log BS_o, the average gradient error $\overline{\Delta G}$ may be determined.

It seems reasonable as a first approximation to assume that if the gradient errors are large, the reproduction quality will be low; while if they are relatively small, the quality will be high; in other words, that the reproduction quality is related in some inverse manner to the magnitude of the gradient errors. Assuming this reasoning to be correct, it may be stated, at least as a first approximation, that

$$Q \propto 1 - \overline{\Delta G}.$$

From a study of the gradient curves for a large number of reproduction curves and the corresponding gradient error evaluations, it is apparent that the average gradient errors may be equal in many cases where, obviously, there are large differences in photographic quality. It seems almost certain that the deleterious effect of a given average gradient error depends greatly upon the distribution of the gradient errors throughout the tonal scale; and from a qualitative examination it appears that for gradient errors of a given magnitude, the best reproduction quality is obtained from an approximately equal distribution of these errors in the shadow and highlight regions. Moreover, even for equal distribution in highlight and shadow regions, the best photographic quality seems to be obtained if the negative and positive gradient errors are approximately equally balanced.

Preliminary trials of the expression shown above made it clear that corrective coefficients should be applied to include the balance of gradient errors between highlight and shadow regions and between negative and positive values. Two corrective coefficients, k_1 and k_2, were therefore formulated, k_1 being the corrective coefficient for the shadow versus highlight balance of gradient errors and k_2 for the balance of the gradient errors between positive and negative values. These corrective coefficients may be explained by reference to Figure 277, in which a typical gradient curve is shown. The integrated areas of the shaded portions are designated by the letters A, B, C, and D.

The two coefficients are defined as follows:

$$k_1 = 1 - \frac{(B + C) - (A + D)}{\log BS_o},$$

$$k_2 = 1 - \frac{(A + B) - (C + D)}{\log BS_o}.$$

In practice, the value of these corrective factors can be determined very conveniently by mechanical integration from the original graph sheets. In each case, the final value can be determined by a single operation by proper manipulation of a planimeter. With these corrective coefficients, the expression for quality becomes

$$Q = (1 - \overline{\Delta G}) \cdot k_1 \cdot k_2.$$

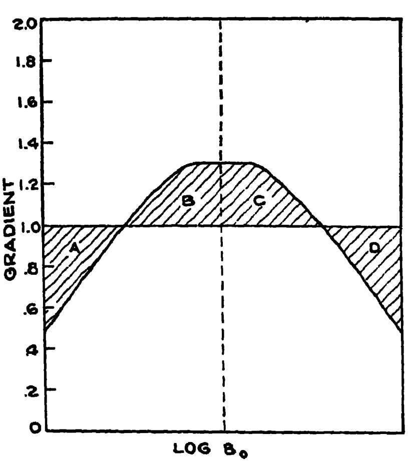

Fig. 277. Typical gradient error curve.

When quality values were computed by this expression for the four series of reproductions used in this work, it became apparent that while agreement between observed and computed values was fairly close, there was still an undue lack of agreement, particularly in the reproduction of medium quality. This situation may be seen from Table LXXXII. In the second column are shown the values of $1 - \overline{\Delta G}$ for each of the twelve prints made on negative material C. These start from a relatively low value and increase progressively to an approximately constant value for the last six prints in the group. It is obvious that these values are not satisfactory indices of reproduction quality. Reproduction No. 3, for instance, for which $1 - \overline{\Delta G}$ is 0.54, is of extremely poor quality, while for reproductions from 8 to 12, inclusive, which are of excellent quality, the values of $1 - \overline{\Delta G}$ are approximately 0.70. In the third and fourth columns of the table are shown the values of the corrective factors, k_1 and k_2, as previously defined, and in the column Z_1 are shown the values obtained by application of these corrective coefficients to $1 - \overline{\Delta G}$. In the column Q_o are the values obtained by the direct judgment of print quality. These are adjusted so that the average of the prints 8 to 12, inclusive, is 100. For the convenient comparison of the values of computed quality with those of observed quality, values of Z_1 have also been adjusted, so that the average for prints 8 to 12, inclusive, is 100, as shown in column Z_2. It is seen that the agreement between computed and observed quality is much better than if computed quality were based on $1 - \overline{\Delta G}$ without the corrective coefficients, which compensate for the unbalance of gradient errors between negative and positive values and between the highlight and shadow regions.

TABLE LXXXII

VALUES OF QUALITY COMPUTED FROM CHARACTERISTICS OF THE REPRODUCTION CURVE NEGATIVE MATERIAL *C*

No.	$1-\overline{\Delta G}$	k_1	k_2	Z_1	Z_2	Q_0	k_3	Z_3	Z_4
1	0.18	0.18	0.65	0.03	5	10	0.17	1	1
2	.33	.33	.48	.05	8	21	.35	3	3
3	.54	.56	.30	.09	14	31	.53	8	8
4	.53	.66	.52	.18	27	41	.64	17	18
5	.62	.85	.95	.48	73	56	.80	58	61
6	.63	.96	.96	.53	80	63	.83	64	68
7	.85	.86	.99	.72	109	81	.78	85	89
8	.74	.99	.94	.68	103	98	.96	99	104
9	.69	.99	.94	.64	97	99	.91	89	93
10	.68	.94	.86	.55	84	98	.97	82	89
11	.76	.99	.99	.74	112	100	.92	103	108
12	.77	.93	.92	.69	104	104	.97	101	106
Average of best five				.66	100	100		94	100

However, the agreement between observed and computed quality (Q_o and Z_2) is still not very satisfactory. The disagreement is greatest in the region of medium negative exposure. The computed values, for instance, for prints 5, 6, and 7 are considerably greater than those from direct observation. An additional factor seems necessary, therefore, to overcome this disagreement. Again, it is logical to find this in an aspect of the gradient of the reproduction curve, such as the density scale of the reproduction, DS_r, which can be measured directly.

The computed quality value, Z_2, of reproduction No. 7 is 109, which is slightly above the average of the five excellent prints, 8 to 12; but, according to the direct observational data, this reproduction is appreciably lower in quality than the average of the five excellent prints. The average gradient error for print No. 7 is very low; and the distribution of the errors was well balanced, which accounts for the high value of computed quality. Table LXXXIII shows that the average gradient of this reproduction is only 0.82 compared with an average of 1.01 for the five excellent reproductions. Moreover, the density scale of reproduction No. 7 is only 1.26, while the average density scale of the five excellent reproductions is 1.54. It appears necessary, therefore, for a reproduction to be adjudged of good quality by the direct experiential estimate, that the average reproduction gradient (for this particular object, at least) should be of the order of 1.0, or that the density scale should approach more closely the logarithmic brightness scale of the object, or both. A third corrective coefficient, based upon average gradient and density scale of the reproduction, is, therefore, desirable. If the contribution of density scale to high reproduction quality is considered first, it seems logical that the percentage of the *unused* density scale of the positive material constitutes an index of the loss in reproduction quality. This leads to a formulation of a corrective factor as follows:

TABLE LXXXIII

COMPARISON OF COMPUTED AND OBSERVED QUALITY VALUES WITH VARIOUS SPECIFIC SENSITOMETRIC CHARACTERISTICS OF THE REPRODUCTION PHOTOGRAPHIC MATERIAL *C*

		Quality			*Reproduction Characteristics*			
No.	Z_2	Q_0	Z_4	G_s	G_h	G_{max}	$\ddot{G}_r$	DS_r
1	5	10	1	0.0	0.74	0.73	0.18	0.28
2	8	21	3	.0	.92	.90	.25	.38
3	14	31	8	.00	.58	1.06	.55	.84
4	27	41	18	.00	.68	1.35	.68	1.04
5	73	56	61	.00	.40	1.55	.85	1.30
6	80	63	68	.10	.29	1.38	.92	1.40
7	109	81	89	.46	.46	1.02	.82	1.26
8	103	98	104	.49	.39	1.43	1.02	1.55
9	97	99	93	.60	.35	1.48	.96	1.47
10	84	98	89	.51	.45	1.57	1.05	1.60
11	112	100	108	.61	.44	1.29	.98	1.49
12	104	104	106	.64	.55	1.48	1.03	1.58
Av.	100	100	100				1.01	1.54

$$k_3 = 1 - \frac{(DS_v - DS_r)}{DS_v}.$$

This reduces to

$$k_3 = \frac{DS_r}{DS_y} = \frac{DS_r}{BS_o}\cdot\frac{BS_o}{DS_y} = \bar{G}_r\cdot\frac{BS_o}{DS_y}.$$

Thus, this corrective coefficient contains empirically both average gradient and density-scale factors.

The values of k_3 are shown in the eighth column of Table LXXXII, and in column Z_3 are the corrected values of print quality. The numbers are again so adjusted that the average of the reproductions 8 to 12, inclusive, is 100, and the final values, in column Z_4, can be compared with those in column Q_o. It is seen that the agreement between observed and computed values is fairly satisfactory.

This method of computing print quality is necessarily open to question, based, as it is, upon a simple hypothesis qualified by a series of three empirical corrections. Nevertheless, the problem is an important one and this attack upon it has real value.

In the application of the theory of tone reproduction to the practice of photography, some physical characteristic of a negative is required as a criterion of the exposure required to print it. Such a characteristic is difficult to choose from theoretical considerations. Because of the limitations of the positive material, theories relating negative characteristics with printing exposure and grade of paper must be founded on an assumption that a definite tonal region—highlight, middle tone, or shadow—of the original object is worthy of the most accurate tone reproduction. Being dependent upon the accepted hypothesis, theories may require negative measurements in any of these regions. Tuttle[25] studied the problem statistically, using large groups of amateur negatives developed as uniformly as possible. These negatives were printed upon papers of three different contrast grades, the exposures of the prints from each negative being varied in steps corresponding to 0.15 log E units. A number of skilled observers selected (1) the best printing exposure for each grade of paper for each negative; (2) the best print from each negative on the best grade of paper. Three possible physical criteria for determining the printing exposure were studied by the same method. These were the maximum density, the minimum density, and the total density (the $\log_{10}$ reciprocal of the total transmission of the picture area). The correlation between these values and the exposure selected as best by the statistical method was then established for the whole group of negatives. In Figure 278 are given curves of the relation between the errors in the exposure by the use of the physical criterion and the frequency with which they occur. These curves show that the total density is the best criterion for printing exposure, the minimum density is second best, while the maximum-density measurement is almost valueless. Recent work suggests that the minimum density is a somewhat more valuable printing criterion than would be expected from the results given in Figure 278.

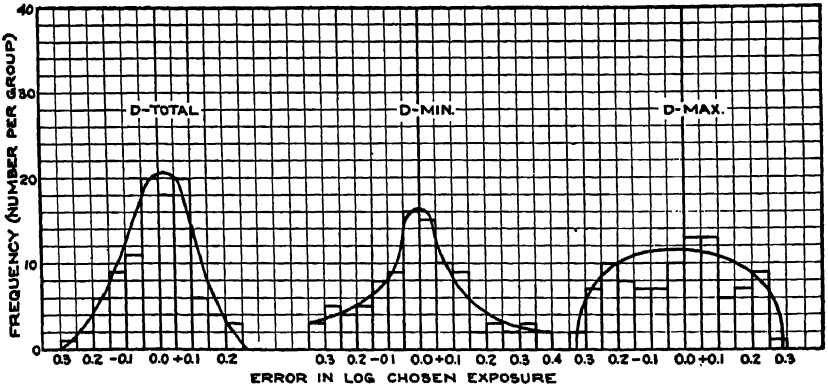

Fig. 278. Relation between the frequency and the size of errors in exposure of prints.

In practice, there is a certain tolerance in printing exposure. This varies appreciably with the subject and was determined by Tuttle by a statistical method similar to that used for determining the best exposure. In Figure 279, the exposure tolerances on a log *E* basis are shown for a number of negatives plotted against their total negative density. The length of the line shows the extent of the tolerance, the numbers being used merely to identify the negative. The diagonal line represents the exposure which would be given to the print, the total density of the negative being used as the criterion. Where the tolerance lines intersect the diagonal, the exposure calculated from the total density will give a print satisfactory to the inspectors; in other cases, a reprint must be made with a revised exposure. The conclusion from these results was that the use of the total density as a criterion gave 94 per cent satisfactory exposures.

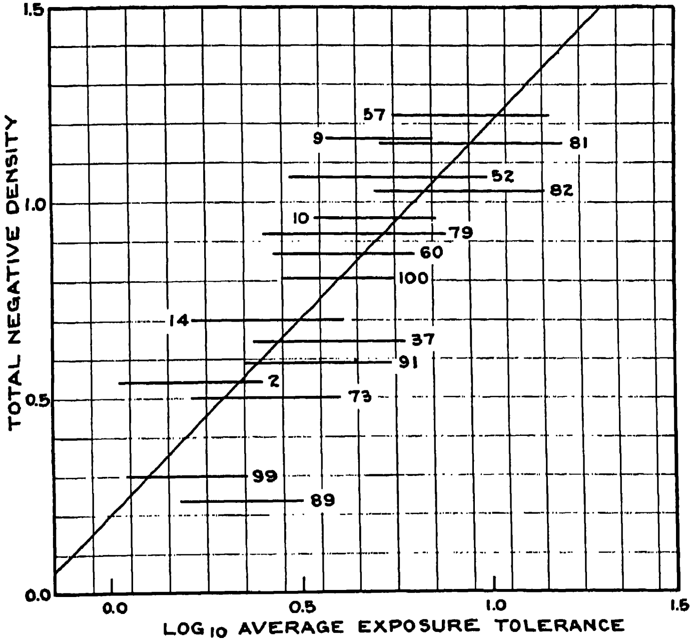

Fig. 279. Relation between total densities of negatives and their exposure tolerances.

An automatic printer based upon these conclusions is satisfactory in practice, the number of reprints necessary being less than for nonautomatic instruments operated by expert printers.

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CHAPTER XXI

THE PHYSICS OF THE DEVELOPED IMAGE

If a very thin layer of emulsion is photographed under a high magnification and then developed and rephotographed in the same position, it will be found that the silver bromide grains have been transformed directly into grains of metallic silver, occupying approximately the same positions, as shown in Figure 280. While the developed grains shown in the photomicrograph occupy *approximately* the same positions as the original undeveloped grains, the positions are not exactly the same. Moreover, the silver grains themselves do not, as a rule, have the same shape as the silver halide grains from which they were formed; the latter are crystals of definite shape, while the former are particles composed of masses of twisted filaments of silver.

In all normal cases, development seems to involve a more or less steady transition from silver halide to reduced silver, accompanied by modification in the shape of the individual deposits.

A matter of some importance in its relation to photographic theory is the possible transference of developability from an exposed grain to an adjacent unexposed grain. It has generally been considered that the grain is the unit in photographic action and that developability is not transferred from one grain to another. Svedberg[1] shows definitely that this was the case for an emulsion in which the grains were almost spherical and of nearly uniform size. On the other hand, there is some evidence that when two or more grains form a clump, they develop as a unit, the reducibility of one grain being sufficient for the development of the entire clump. This effect is reported by Trivelli, Righter, and Sheppard[2] to be very marked for one particular emulsion. The grains were of a very extended range of sizes; and, in particular, a large proportion were thin polyhedral grains, practically flat plates of diameters up to ten or twelve times their thickness. The variation in grain pattern clearly accounts for the difference in behavior; and, as ordinary emulsions run the gamut between these extremes,[3] it is evident that the extent of infection varies from substantially zero to a considerable amount.

The form and constitution of the developed silver grains have been studied by many workers, but until recently they had not been elucidated because the resolving power of the microscope is insufficient to enable the structure to be seen. Scheffer[4] described the growth of filaments of silver from bromide grains during development; but since this phenomenon was not observed by other workers except in the case of very thin emulsion coatings, it was believed that the gelatin structure in Scheffer's emulsions was weak and probably contained fissures. Hodgson[5] reported that, whereas Seed Graflex plates developed with pyro gave irregular grains of silver, an experimental emulsion gave silver grains having the same contour as the silver bromide from which they were formed. Davidson[6] measured the average grain-size increment of silver bromide crystals in different emulsions upon development and found that the percentage increase bears a linear relationship to the speed of the emulsion. He also noted that the appearance of the silver grains varies according to the developer. In particular, *p*-aminophenol was found to give spongy grains. Photomicrographs published by Wightman and Trivelli[7] show very clearly the difference in appearance of silver grains produced by different developers. With a hydroquinone developer, the silver grains had roughly the same contour

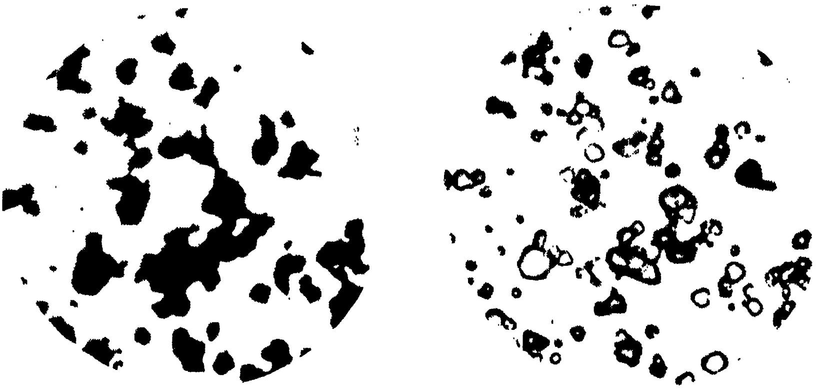

FIG. 280. Developed and undeveloped emulsion grains.

as the silver bromide crystals from which they were produced; a metol developer gave some distortion; amidol gave considerable distortion; *p*-phenylenediamine gave a fluffy deposit; and a tenth-strength metol-hydroquinone developer gave a very porous deposit.* In the same article, an account is given of a motion-picture study of development, which showed that development often starts at several places on each grain. The technique of motion-picture photomicrography was improved by Tuttle and Trivelli,[8] so that a 1.8-mm. oil-immersion objective could be used for photographing the developing grains. It was found that development with metol started from centers on the grain which vibrated continually during its conversion to metallic silver. The grain was seen to throw out threadlike streamers, which were likewise in rapid movement. Frieser[9] has also made motion pictures of the darkening by photochemical decomposition and by development of silver bromide crystals and observed that slowly acting developers cause "needle-shaped masses" of silver to grow from the crystals. Although the silver grains produced by hydroquinone development have practically the same external shape as the silver bromide from which they are formed, it is possible to observe the presence of a fine structure in them by using a microscope adjusted to give the maximum possible resolving power by darkfield illumination.

Somewhat greater resolution can be obtained by the use of ultraviolet light. F. F. Lucas† of the Bell Telephone Laboratory has obtained photomicrographs of developed silver grains with the cadmium 275 mμ line as a source of light and using a quartz monochromat objective with a numerical aperture of 1.25. The resolving power of this combination is 110 mμ, as against 160 mμ for the best results obtainable with ordinary microscopic equipment. One of these photomicrographs is reproduced in Figure 281. It shows the appearance of a fine-grain emulsion after it had been given a brief exposure to light, developed, and fixed. A filamentary structure can clearly be seen in the grains, confirming, though with insufficient resolution, the structure shown by the electron microscope.

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* For an account of Loveland's work on the form of the grains produced by different developers, see Chapter XI, p. 463.

† Private communication.

By the use of the electron microscope, the structure of developed silver has been elucidated completely (Chapter VIII, p. 311). The electron microscope has an effective resolving power of the order of 5 mμ and, in addition, possesses two important advantages over the optical microscope. The first is that its cone of illumination is about ½°, compared with the 121° cone of a 1.32 N.A. microscope objective. This means that, whereas the electron image is practically an orthographic projection of the object, the optical image is a combination of all the orthographic projections within a solid cone of 121°, and all objects at the limit of optical resolution tend to appear spherical. The second advantage of the electron microscope lies in its considerable depth of field, which is one or two microns, or several hundred times the limit of resolution, whereas with the optical microscope at its highest resolution, the depth of field is approximately the same as the resolving power. von Ardenne[10] has taken advantage of the considerable depth of field of the electron microscope to equip it with a 12° rotation of the object

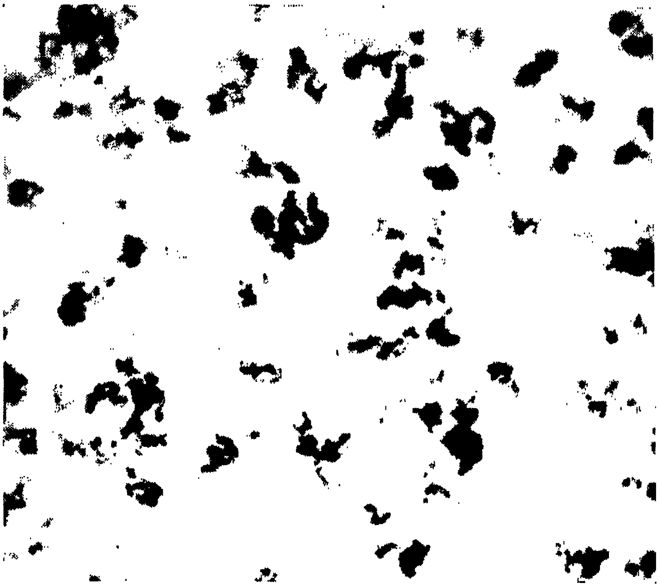

FIG. 281. Photomicrograph by ultraviolet light of developed grains (× 3000). Courtesy of F. F. Lucas, Bell Telephone Laboratories.

holder so that stereoscopic pairs of images are obtained. He published stereoscopic electron micrograms of developed silver grains which show that the silver is a tangled mass of fibers having a thickness of 10 to 15 mμ. C. E. Hall of the Kodak Research Laboratories applied an electron microscope built ac-

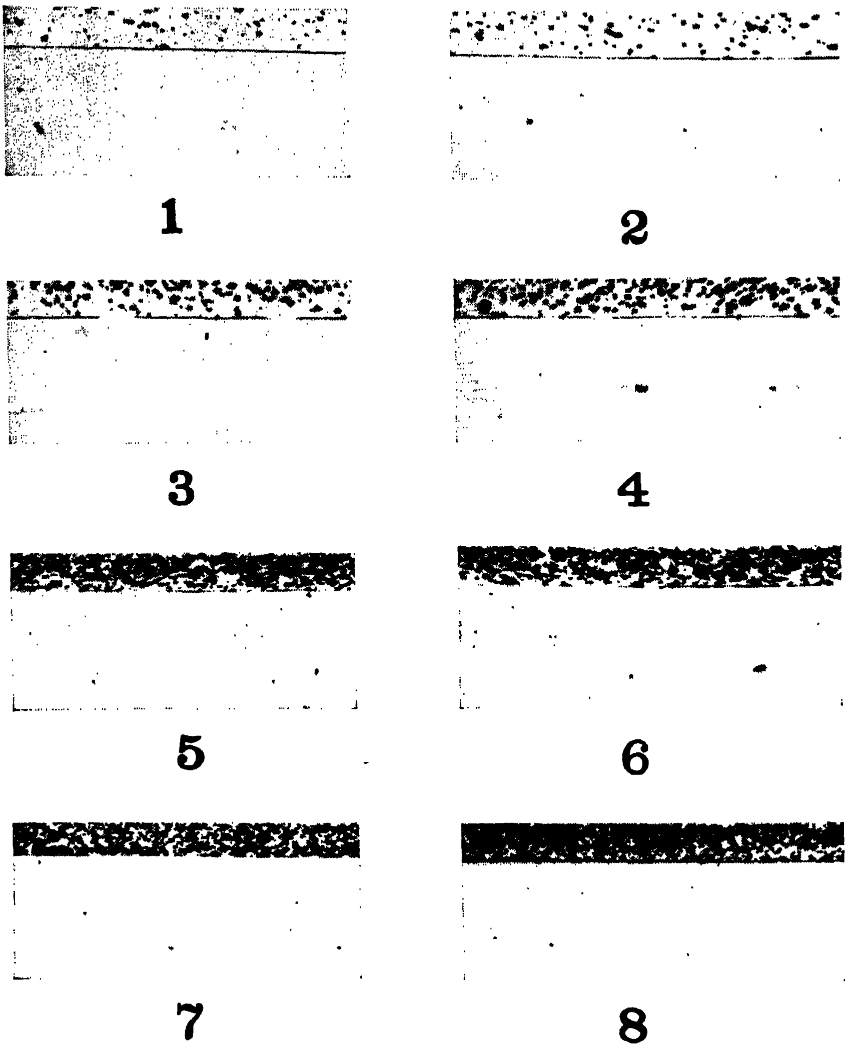

Fig. 282. Series of cross sections (dry) showing growth of image with exposure.

cording to the design used by E. F. Burton[11] to the problems of development, with the results described in detail in Chapter VIII, p. 311. From these results, it is seen that the developed silver grain consists of a spongy mass of silver fibers. The degree of compression of the sponge naturally depends on the rigidity of the surrounding gelatin in an emulsion which is being developed. The rigidity of the surrounding gelatin depends on its degree of swelling and on the rate of conversion of the silver bromide crystals to metallic silver. It is not unlikely that with very rapid development the swollen gelatin is actually liquefied in the vicinity of the grains before the liberated heat is conducted away.*

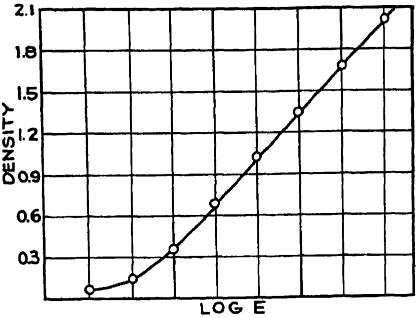

FIG. 283. Characteristic curve from strip of which sections are shown in Figure 282. Circles indicate densities of sectioned parts.

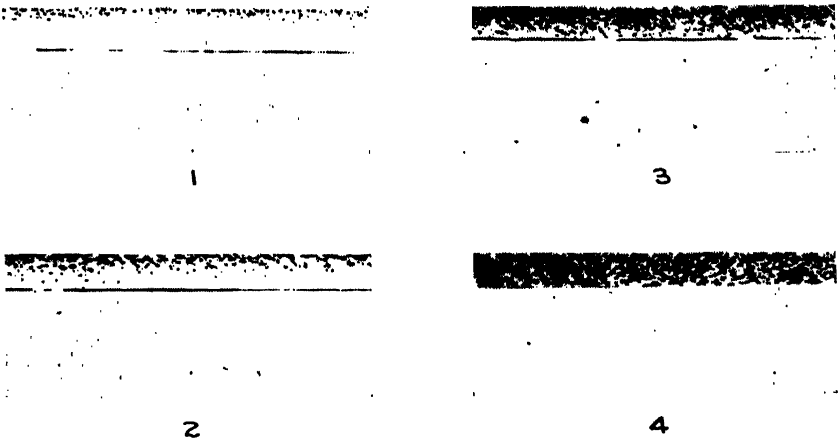

FIG. 284. Series of cross sections showing growth of image with development.

The distribution of the image in the depth of the film was studied by Hodgson,[5] and Figure 282 from his paper shows sections cut through developed images corresponding to the densities on the characteristic curve indicated in Figure 283. Figure 284, from the same paper, shows the growth of an image with development. It is seen that the image starts to develop at the surface and penetrates downward as development is continued, so that when development is complete the image is distributed throughout the entire depth of the emulsion. This, however, depends upon the wave length of the light. With the extreme ultraviolet, which is very strongly absorbed by the emulsion, the image is confined to the surface, while with X rays, which are but slightly absorbed, the distribution depends merely upon the sensitivity of the grains, regardless of their depth in the coating. With light that is partly absorbed by the emulsion, the image tends to be denser at the surface in proportion to the absorption.

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* See Chapter VIII for a discussion of the chemical reactions by which this filamentary structure may be produced.

GRANULARITY AND GRAININESS

To the eye, a developed photographic image appears to be homogeneous; but if it is examined under a moderate magnification, the grains of silver will be seen to be welded into clumps and to overlap each other. Thus, when the image is viewed by transmitted light, agglomerations of the grains separated by spaces within the emulsion are seen, approximately six clumps being piled over one another. This overlapping pattern of grains is exhibited in Figure 285, which shows a horizontal section of the image layer in comparison with a vertical section through the same film.

The inhomogeneity of the image just described, to which the term *granularity* is applied, is significant to the practical photographer because it sets a limit of magnification beyond which an enlargement is not pleasing. An enlargement made from the negative at too high a magnification gives an unpleasant impression of *graininess.** This phenomenon may appear at a magnification of only a few diameters in the case of very fast emulsions—long before individual grains or even clumps can be distinguished.

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* Inasmuch as the proper magnification of the image is determined by perspective considerations, it would be preferable to blame the graininess upon the selection of an excessively small scale in making the negative. It must be remembered that the correct viewing distance for a contact print is the focal length of the lens; for an enlargement, it is this focal length multiplied by the magnification introduced by the enlarger.

The most obvious procedure for measuring graininess would be to make a series of enlargements at different magnifications

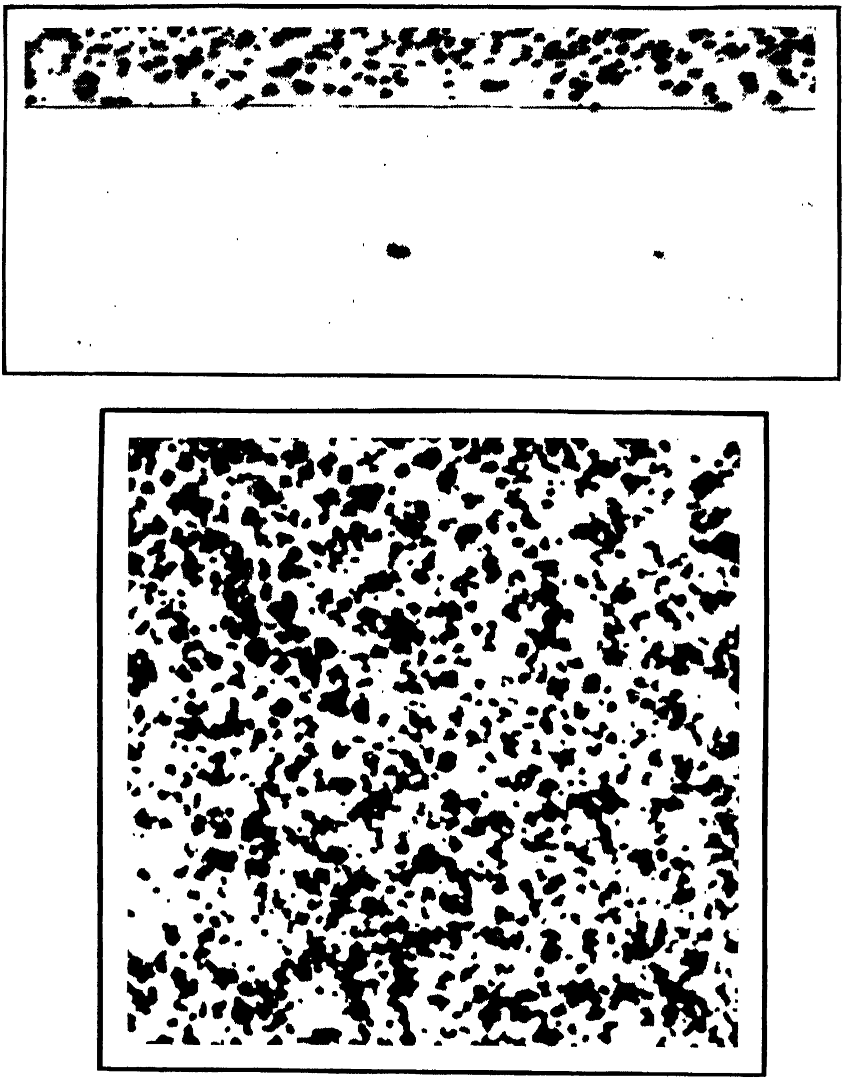

FIG. 285. Photomicrographs of grain deposit: Above, cross section; below, horizontal plan.

and then observe them from a fixed distance to determine the magnification at which graininess just disappears. Although this procedure or a similar one is occasionally followed, it is both expensive and time-consuming because γ's and densities must be accurately matched if the test is to be significant. A simplification would be to make a single enlargement and then evaluate its graininess on the basis of the blending distance, where the phenomenon just disappears. Even then, however, the intermediate steps represented by the intervention of the degree of enlargement into the procedure are not eliminated, and the evaluation is profoundly affected by the conditions under which the enlargement is made.

One of the earliest and still one of the most satisfactory of the direct methods is described by Jones and Deisch.[12] Their instrument consisted of a microscope system which projects a magnified image of the photographic deposit on a screen. The observer views the screen in a mirror attached to a carriage that runs on a track, and, by moving the mirror, he can vary the distance from his eye to the image of the screen. The assumption is made that the graininess of a given material is proportional to the blending distance, provided that all the factors upon which depends the ability of the eye to distinguish lack of homogeneity are constant. It is evident that measuring the blending distance for an image of constant magnification is equivalent to measuring the magnification for a predetermined blending distance.

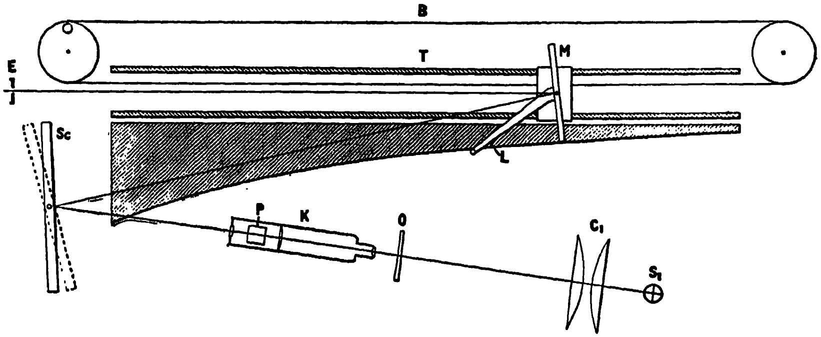

FIG. 286. Diagram of Jones-Deisch instrument for measuring graininess.

A diagram of the essential parts of the instrument constructed by Jones and Deisch is shown in Figure 286. Light from a ribbon-filament lamp, S_1, passes through the substage condenser, C_1, and the photographic material, O, placed on the stage. The microscope, *K*, projects a magnified image on the magnesium carbonate screen, *Sc*. The observer, by placing his eye at the artificial pupil, *E*, sees the image of the screen reflected in the mirror, *M*. This mirror runs along the track, *T*, and is controlled in orientation by the template, *L*, which maintains the mirror in such a position that the screen is always visible to the observer. The carriage for the mirror is driven forward and backward by means of the tape, *B*, which is provided with a scale indicating the distance of the mirror from the observer. From the reading of the scale, the total distance between the eye of the observer and the image of the screen seen in the mirror can be calculated. In the instrument described, the track was of sufficient length to permit this distance to be varied from two feet to more than sixteen feet. The Lummer-Brodhun cube *P* was introduced to send a second beam into one half of the field for comparison.

Assuming the visual acuity of the eye of the observer to remain constant, the procedure would be to place the photographic material on the stage of the microscope and move the mirror out slowly until the screen appeared to blend into a smooth area. The scale would then be read at the point where the sensation of graininess vanished. The optical distance from the eye to the screen for this position would then be a direct measure of the graininess of the material. Thus, it could be said that a material with a blending distance of six feet was twice as grainy as one with a blending distance of only three feet.

It is well known, however, that visual acuity depends upon a number of factors, the principal ones being the adaptation level of the eye, the contrast and color of the field of view, the general physiological condition of the observer, and such other uncertain conditions as fatigue and practice. Moreover, visual acuity is continually changing. To eliminate the effect of such changes on the graininess measurements, the following scheme was adopted: In computing the graininess of a given photographic material, its blending distance was divided by the corresponding distance determined for an engraver's half-tone screen. This ratio of the two distances was taken as a numerical measure of the graininess of the photographic material. The same half-tone screen was used throughout, and in this way the ratio of the two blending distances was found to remain constant, although both distances might vary considerably from day to day. It was even found possible for two observers to agree on the graininess of a photographic material when the blending distance according to one observer was very different from that determined by the other.

The greatest uncertainty in graininess measurements arises from the circumstance that the grain distribution is random and hence nonuniform. When the pattern is uniform, as in the case of a half-tone screen, the blending distance is quite definite; in the case of a photographic deposit, the transition is more gradual and, indeed, close observation will detect two states. In the words of Jones and Deisch:

> "With the mirror close to the eye, the primary aggregates are easily resolved. As the mirror is driven out these disappear, and irregular patches are formed. The last are caused by a certain clustering of the aggregates, which makes itself evident by an increase of density in the clusters. On further driving out the mirror, only diffuse markings can be seen, and finally these disappear altogether. These various changes in the appearance of the field are not, however, in any way abrupt, and some difficulty is encountered in determining upon and retaining one definite stage as a criterion. . . . It was found by a comparison of . . . readings that those taken using as a criterion the point marking the first step in the fusing of the image of the photographic deposit, the change from aggregates to clumps, show much greater correspondence with each other than those taken at the disappearance threshold; hence, this point was adopted as a criterion for all subsequent readings."

Few later writers are as explicit in stating whether the upper or the lower limit of magnification is being considered.

Several improvements made in the details of the Jones and Deisch technique are described in a paper by Hardy and Jones.[13] As a result of these modifications, it was found possible to measure the graininess of a photographic material with such precision that the average deviation of the graininess factor for a single observation would not exceed 3 per cent under ordinary conditions.

Because of the artificial nature of the procedure adopted, it was necessary to prove that graininess values as measured with the instrument correspond to the graininess as already defined and as understood by the photographer. For this purpose, a typical negative material was given a graded series of exposures in a sensitometer and developed in the usual way. The result was a negative consisting of a series of steps of varying density. Since the graininess of the material was too low to be perceptible by the naked eye, photomicrographs were made of each step, the same exposure and time of development being given to each. Prints were then made, again with the same exposure and development for all. A photograph of these prints mounted together in the proper order is shown in Figure 287. Since the photomicrographs were made under identical conditions of exposure and development, this figure represents the appearance of the original negative when magnified nearly one hundred diameters. It is seen that the maximum graininess occurs in the neighborhood of the third lightest step. This can easily be verified by placing the page at such a distance from the eye that the graininess in all the other steps disappears. As the observer approaches the illustration, it becomes evident that the graininess diminishes on either side of the maximum, as would be expected, since photographic deposits of zero density or of infinite density obviously cannot have any apparent granular structure. The negative, from which the photomicrographs were made, was then placed in the graininess apparatus, and the graininess factor * of each step was determined in the usual way. The value of the graininess factor for each step plotted as a function of the corre-

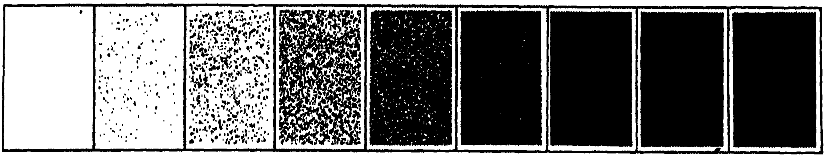

FIG. 287. Enlargements showing the relation between density and graininess.

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* The graininess factor is the product of an arbitrary constant and the ratio of the distance of the negative to the blending distance of the half-tone screen. Thus, if K is the arbitrary constant, D_1 the distance for the photographic material, and D_2 the corresponding distance for the half-tone screen, the graininess factor, G, is expressed by:

$$G = K\frac{D_1}{D_2}.$$

The arbitrary value of K chosen was 508, and the half-tone screen has 500 lines to the inch. The details of the other conditions are given in the original paper.

sponding density is shown in Figure 288, from which it is evident that the curve describes accurately the graininess of the material. The graininess is at a maximum in the neighborhood of the third step and falls off on either side, as before.

There is a good *a priori* reason for the maximum graininess to occur somewhere near an optical density of 0.3. In this case, the total area occupied by the grains themselves is equal to the total area of the spaces between the grains. It is known that, when a number of uniformly spaced parallel lines are ruled in black ink on a white card, the lines can be resolved at the greatest distance when they are equal in width to the white spaces between them. The reader can prove this for himself by turning to Figure 328 on page 899 and determining the relative blending distances of the various sets of lines. For somewhat similar reasons, the maximum graininess should occur when the total grain area is equal to the total area of the interstices. The maximum graininess is usually at a somewhat higher density, but the agreement with expectation is sufficient to constitute a secondary confirmation of the validity of this method of measuring graininess.

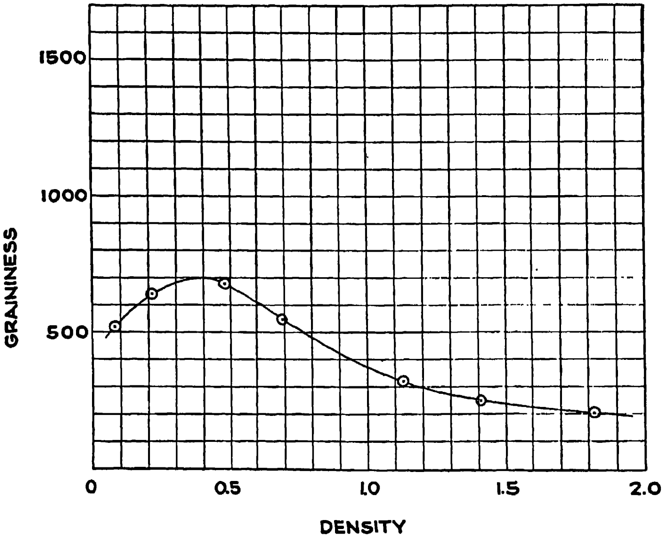


FIG. 288. Graininess-density curve for constant sample illumination measured on Jones-Deisch instrument.

The instrument described above is cumbersome and, owing to the presence of the diffusing screen, the maximum obtainable field brightness is low. Both disadvantages were overcome by Lowry[14] in an instrument in which the observer viewed an aerial image formed by a lens. A diagram of this apparatus is shown in Figure 289. The sphere, *S*, is illuminated by means of one to thirteen flashlight lamps, *B*. Light from the sphere passes through the photographic plate or film at *X* and through a positive lens, L_5, placed at a distance from the plate which is always less than the focal length of the lens. This lens, therefore, forms a virtual image of the deposit, which is seen at the artificial pupil, *Y*. A homogeneous comparison field is formed by means of the prisms, P_1 and P_2, the lenses, L_3 and L_4, and the mirror, *M*. The mirror is of stellite, ground and polished to a fine edge, *D*; and it is this edge that forms the dividing line in the photometric field. The intensity in this field is controlled by means of the neutral gray wedge, W_1; W_2 serves primarily for

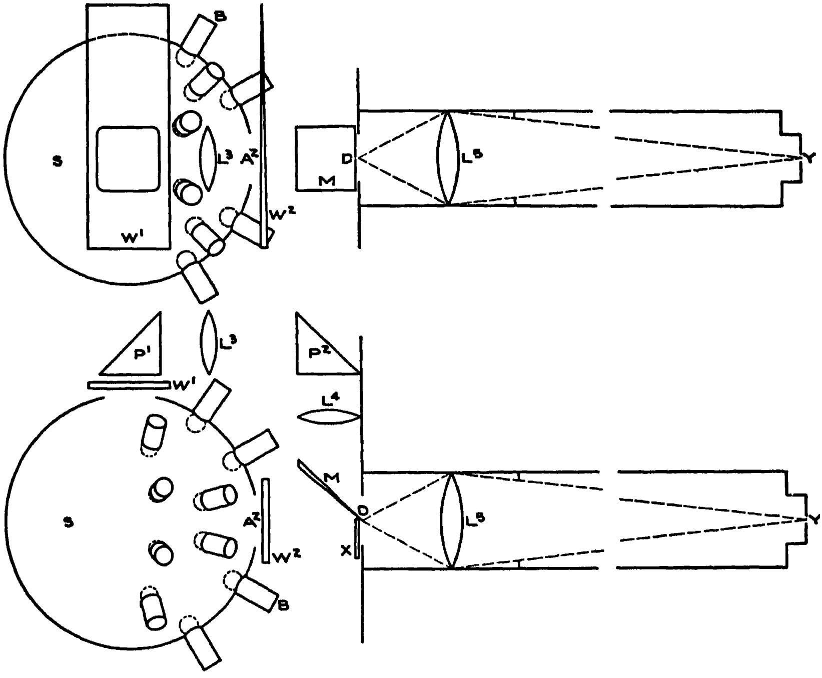


FIG. 289. Diagram of Lowry instrument for measuring graininess.

setting the zero of the instrument. Some of the incidental advantages of the apparatus are that the brightness of the field is sufficiently high to enable readings to be made without difficulty in a moderately lighted room; the necessity for dark-adapting the observer's eye and the accompanying inconvenience and fatigue of working in a darkened room are thus obviated. The wedge, W_1, is calibrated so that the density of the deposit under examination can be read simultaneously with the determination of graininess, an additional operation thus being saved. Furthermore, the field subtended at the eye by the lens remains practically constant throughout the entire scale of the instrument, which is not the case for the earlier apparatus.

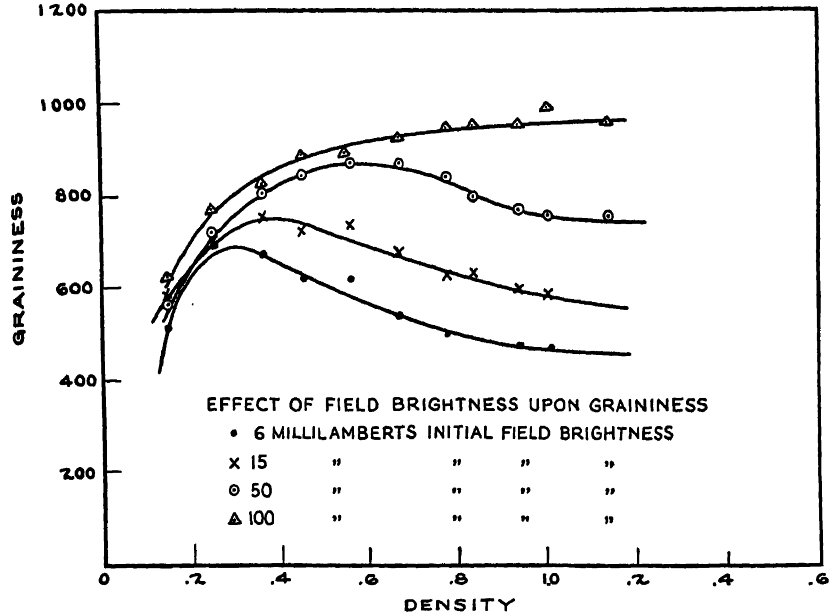


FIG. 290. Graininess-density curves for constant sample illumination measured on Lowry instrument.

Some of Lowry's curves are reproduced in Figure 290, in which the brightness values are those which obtain before the sample is inserted; the field brightness as seen by the observer diminished as the sample density increased. These curves are similar to those found by the earlier investigators at low levels of field brightness. As the brightness level was raised, however, the density for maximum graininess increased, as did the graininess factor itself at any given density. This increase must, of course, cease at some density because an infinitely dense deposit must have zero graininess. The diminution of graininess with increase of density for the lower curves is probably attributable to the decreasing acuity of the eye at low brightness levels. The failure of the upper curve to droop within the density range studied can be attributed to the brightness of the interstices between the grains. As the density increases, the granular pattern becomes coarser because more and more of the interstices are filled up, but the decreasing visual acuity more than compensates unless the sample illumination is high.

If the illumination on the sample is not held constant but is increased to compensate for the density of the sample, the curves of Figure 291 are obtained. This shows that the faster materials are more grainy, in general, but, more surprisingly, that a linear relation exists between the graininess and the density of a given emulsion. Moreover, the rates of increase of graininess are in the same order for the emulsions tested as the values of graininess themselves at any selected density.

The photomicrograph shown in Figure 285 suggests the making of a series of photomicrographs of arbitrarily selected standards covering the entire graininess gamut with which a photomicrograph of the sample can be compared. Reinders and Beukers[15] attempted to put this method on a quantitative basis by determining the magnification of the sample required to match a certain standard. A somewhat similar procedure, described by Conklin,[16] is to examine the sample and the standard directly in a special comparison microscope so that the magnification of both can be varied in opposite senses until the two match in graininess. An ordinary comparison microscope can be used at a magnification of about seventy-five times to locate the sample in a series of arbitrary standards or to compare two samples with each other. The difficulty in all procedures of this general nature is that the graininess pattern of the sample may be quite different from that of any standard even though the standards themselves form a consistent, ordered series without wide gaps. Moreover, experience shows that the results thus obtained must be interpreted with caution.

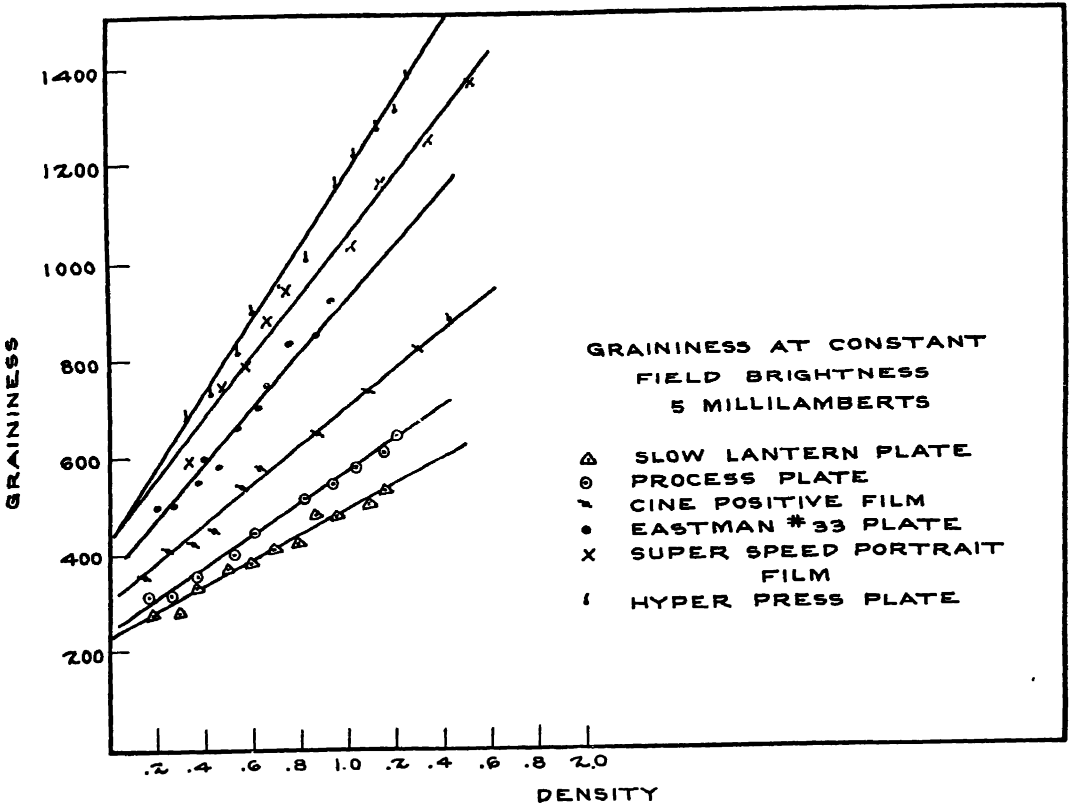


FIG. 291. Graininess-density curves for constant field brightness measured on Lowry instrument.

Inasmuch as both graininess and the Callier coefficient Q (Chapter XVII, p. 642) depend upon the granular structure of the deposit, it is natural to suggest that the latter, which is readily measurable, is a criterion of the former. Threadgold[17] suggested that a measurement of the value of Q could be used for the determination of graininess; and he gives the illustration shown in Figure 292, where straight lines obtained by plotting the relation between the log $D//$ and log $D\#$ are given for four different photographic materials. The use of Q for measuring graininess was studied further by Küster.[18] Using a Martens polarization photometer for the density measurements, he found satisfactory agreement between graininess and the Callier coefficient. His expression for graininess was

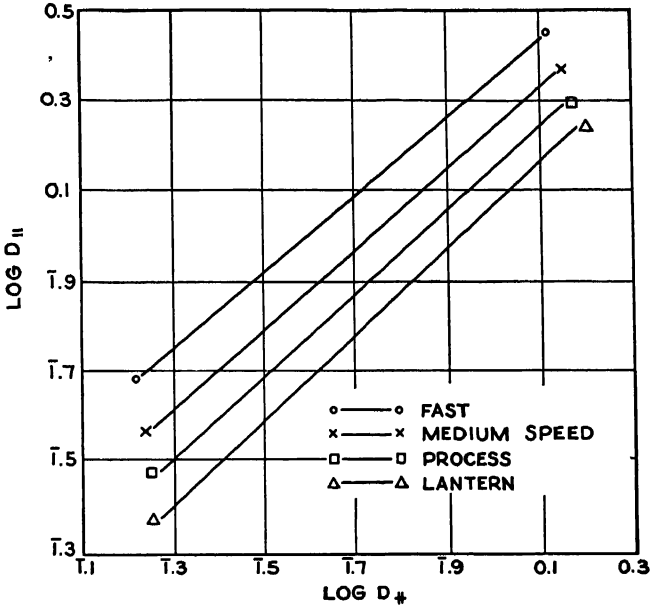


FIG. 292. Relation between specular and diffuse densities for various materials (Threadgold).

$$K = 100 \log \frac{D//}{D\#} \quad \text{when } D\# = 0.5.$$

In 1934, Eggert and Küster[19] published details of further work on the method, and their results were criticized by Narath.[20]

Eggert and Küster, however, point out the origin of Narath's difficulties and conclude that the method gives perfectly reproducible values when operated under proper conditions and is the simplest so far proposed for the measurement of graininess. According to Eggert and Küster,[21] the value of Q has a direct relation to the average diameter of the silver grain; and they concluded that $d = C \log Q$, where d is the average diameter of the developed grains and C is a constant depending upon the apparatus.

Despite the work which Eggert and Küster did, the validity of the Callier coefficient as a criterion of graininess cannot be said to be established. Thus, Hansen and Keck[22] determined the coefficient for seven emulsions and then determined the corresponding graininess values with an apparatus similar to Jones and Deisch's. The results, when plotted as in Figure 293, show a nearly linear relation. On the other hand, Lowry found only the roughest sort of correlation in the case of seven emulsions; and in one instance the result was contradictory, as Figure 293 also shows. Eggert and Schopper[23] then studied (*a*) a fine-grain plate and (*b*) a coarse-grain one, as well as (*c*) a print of (*b*) on (*a*). They found experimentally that the Callier coefficient of (*c*) was the same as that of (*a*), and they attributed this circumstance to the correlation with respect to grain size because the same grains are involved. On the other hand, subjective observations showed that (*c*) was more grainy than (*a*) because the interstices between the grains were larger, as will be discussed below. On the whole, it seems that under certain circumstances the Callier coefficient may be a measure of graininess, but the published experiments to date indicate that it is not applicable when the distribution of the grains is of appreciable importance compared with the diameter of the grains (or clumps of grains) themselves.

A more elaborate method of evaluating granularity, and one that takes grain distribution as well as grain diameter into account, is to make a trace with a microdensitometer. Difficulty then arises in correlating the granularity characteristics thus displayed with the subjective impression of graininess. However, in astronomical and spectroscopic work, granularity alone is involved because the final result is usually a microdensitometer trace; and the chief effect of granularity is to produce irregular displacements of the trace. Thus, Figure 294, from a paper by Dunham,[24] shows enlargements of iron lines photographed with

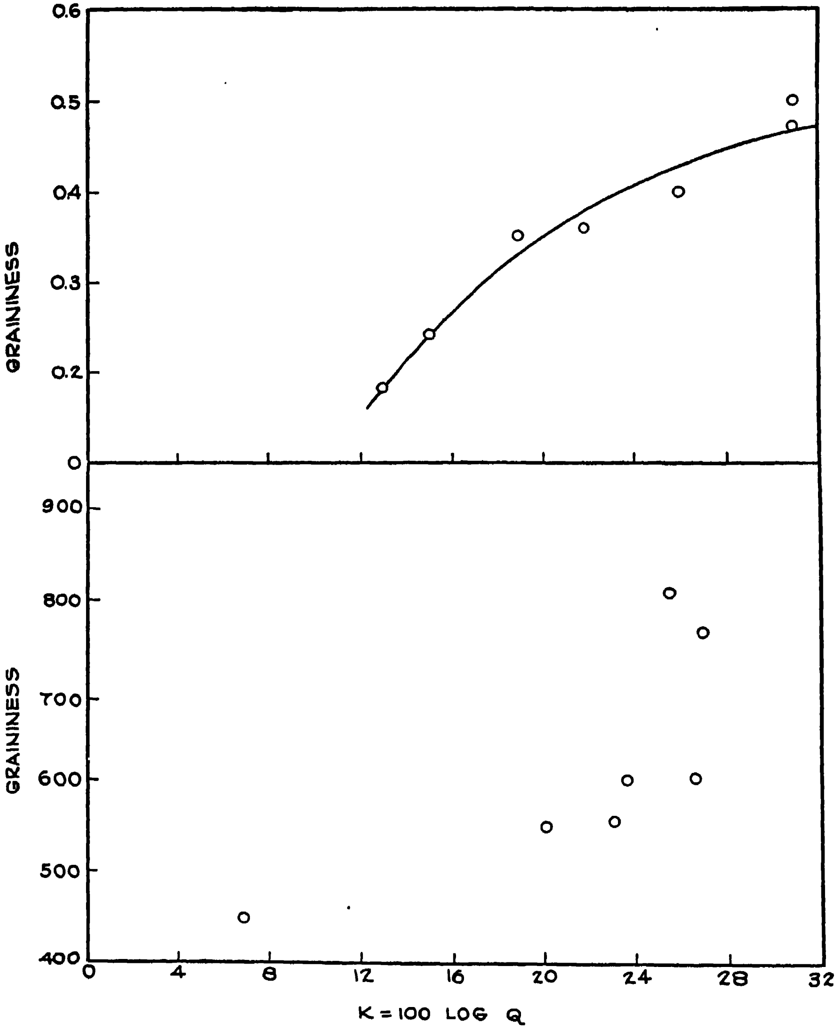


Fig. 293. Relation of graininess to the Callier coefficient, Q: Above, Hansen and Keck; below, Lowry.

a stellar spectroscope upon an Eastman Process plate and an Eastman 40 plate, as well as microdensitometer traces of the same spectra. It is seen that, while the traces from the process

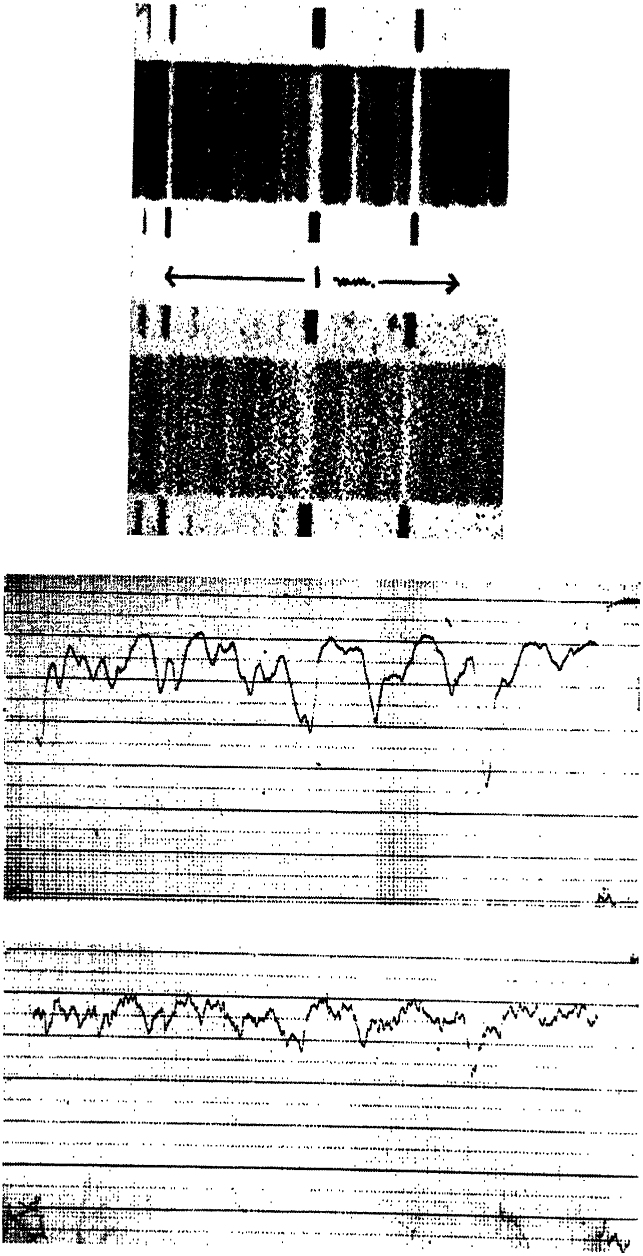


Fig. 294. Enlargements of iron spectra and microdensitometer traces of them: Above, Eastman Process Plate; below, Eastman 40 plate.

plate show only a few small irregularities, the trace from the Eastman 40 is badly broken up. Dunham has suggested that the relative granularity of emulsions could be shown readily by microdensitometer traces of regions uniformly blackened to a density of 0.3. The magnitude of the effect depends upon the setting of the instrument. The slit of the microdensitometer in the case just cited is 0.5 mm. long and 5 μ wide, a customary setting in astronomical work. Traces of this nature on five different types of emulsion designed for spectroscopic use are shown in Figure 295.

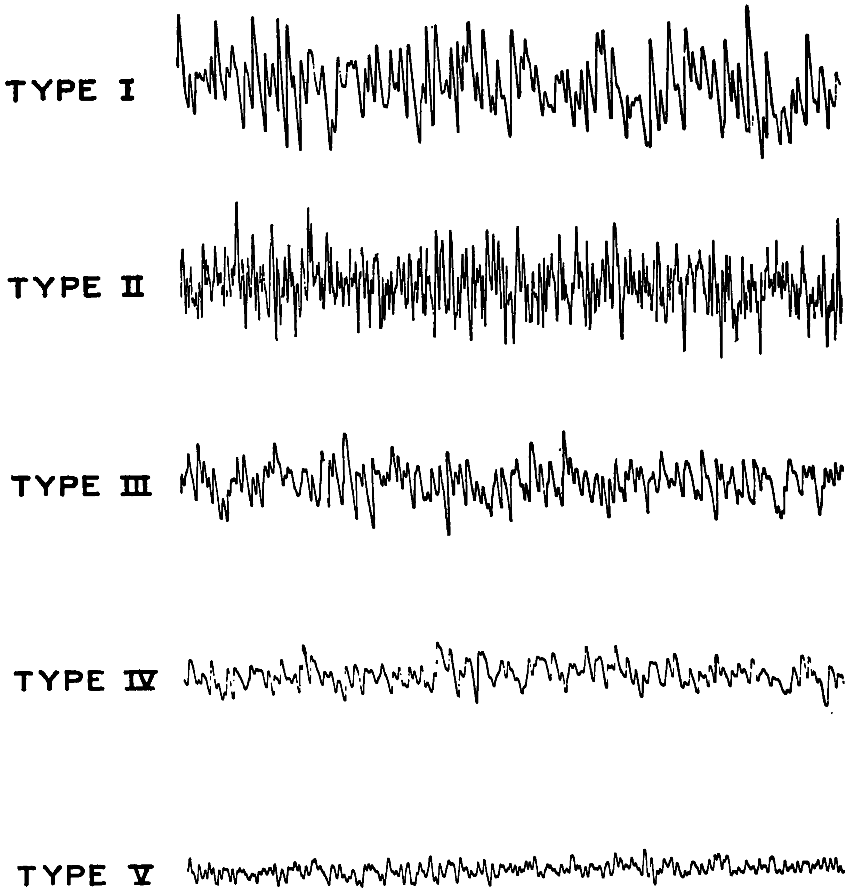


Fig. 295. Microdensitometer traces showing the granularity of certain Eastman spectroscopic plates.

To consider how such a microdensitometer trace might be evaluated subjectively, a study of the statistical density variation of a photographic deposit is desirable. If the grains of a deposit having a given density and brightness were of uniform size and were distributed uniformly, the graininess as judged from the magnification required to make the inhomogeneity in any way perceptible would depend merely upon the grain size and the grain concentration, the latter determining the grain spacing, assumed to be uniform. But, as a matter of fact, the grains are statistically distributed in space so that elementary cells of uniform size contain quite different numbers of grains. This clearly superposes a coarser pattern upon the one made by the grains themselves and thus increases the graininess. Moreover, the scale of this *statistical-distribution* pattern depends upon the size of the grains. It is clear that the frequency distribution of the grains among the cells is constant in magnitude, as the grain size varies, only if the scale of the grid of cells is proportional to the grain size.

If the grains of emulsions in general were uniform in size, it might not be too difficult to deduce the characteristics of the microdensitometer trace from the frequency distribution of the grains. Most negative emulsions have a wide range of sizes, however. As a result of such obstacles, most workers content themselves with relating the microdensitometer trace to some kind of graininess parameter.[25] It would be desirable to express graininess by a single parameter, and the mean deviation in density or transparency might be adopted. This direct method has been used somewhat, but it can be misleading. Thus, the mean deviation can be the same for a few large deviations or many smaller ones, whereas the former sample would undoubtedly appear to be the grainier. Instead, it is assumed merely that the deposit is characterized by a certain *graininess constant*, G. Then a probability P $(\Delta, d\Delta)$ exists that a cell having an elementary area a has a density, different from the mean density D of the material, within the range $(\Delta, d\Delta)$; let this probability depend upon a, Δ, $d\Delta$, and G alone. Then, Selwyn[26] shows, by means of dimensional analysis and the theory of differentials, that

$$P(\Delta, d\Delta) = \sqrt{\frac{a}{\pi G^2}}\, e^{-\Delta^2 a/G^2} d\Delta. \qquad (1)$$

This means that the plot of the distribution of density deviation Δ from the mean value D is similar to the familiar Gaussian error curve. Thus, the density distribution is described by some function of $G/\sqrt{a}$. The standard deviation for equation (1), which is defined as the root-mean-square of the individual values of Δ, is given by equation (2):

$$\sigma = \sqrt{\frac{G^2}{2a}}. \tag{2}$$

This, again, is a function of $G/\sqrt{a}$ alone, and as it indicates the "breadth" of the distribution curve, the not unexpected result is obtained that graininess is a function of the dispersion of the individual deviations.

Suppose, now, that two samples, when compared by the Jones-Deisch method previously described, appear equally grainy. Then, the standard deviation over a certain elementary area α of the retina is the same in each case, although α corresponds to an area a_1 for one sample and a_2 for the other, the over-all magnifications being M_1 and M_2, respectively. The graininess constants are G_1 and G_2, so

$$G_1M_1/\sqrt{\alpha} = G_2M_2/\sqrt{\alpha}$$

or, since $M \propto 1/d$,

$$G_1/G_2 = d_1/d_2. \tag{3}$$

This gives some theoretical basis for the assumption on which the Jones-Deisch method was based.

To correlate equation (1) with the microdensitometer trace, let the value of a represent the area of the sample covered at any instant by the scanning beam. The amplitude of each deviation from the mean is, then, Δ, and the distribution curve of the individual values of Δ should represent the function $P(\Delta, d\Delta)$. Selwyn[27] investigated this, making a statistical study of the deviations for three different emulsions and six different scanning-beam diameters. The emulsions were as follows:

A_1 Process	Density 0.37
A_2 Process	Density 1.33
B_1 Medium Speed	Density 0.33
B_2 Medium Speed	Density 0.75
C_1 High Speed	Density 0.37
C_2 High Speed	Density 1.20

The deviations in each case were plotted on probability paper, on which a true Gaussian distribution would be rendered as a straight line; and the value of $G/\sqrt{a}$ was determined from the

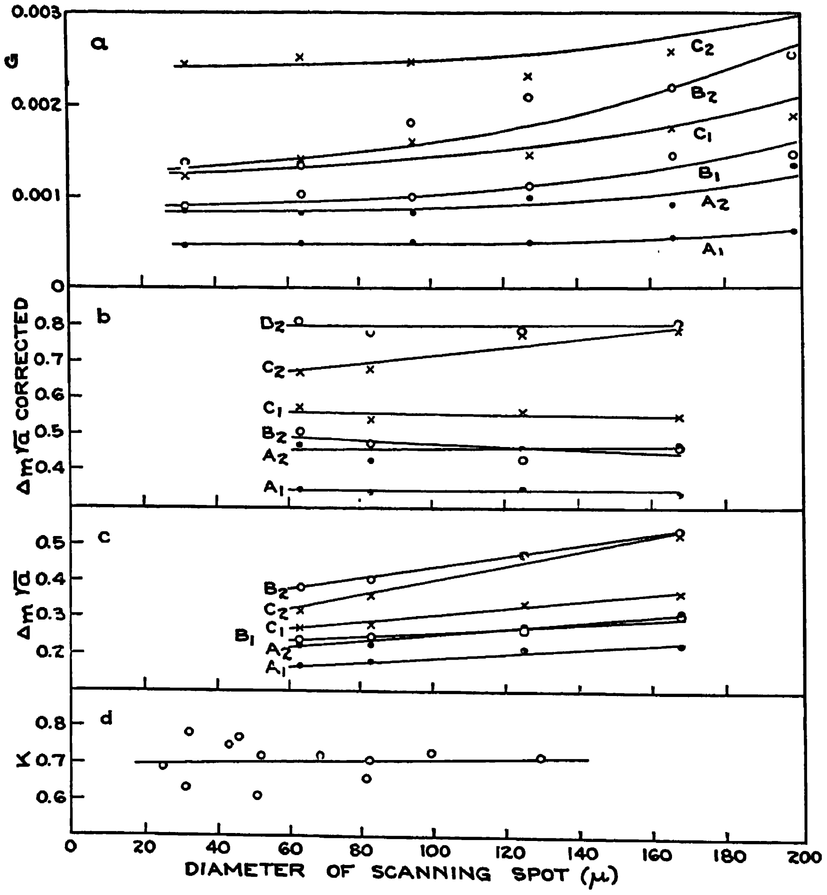


FIG. 296. Variation of granularity with diameter of scanning spot: (a) Selwyn, (b) van Kreveld, (c) van Kreveld, uncorrected for sluggishness of rectifier, and (d) Hansen and Keck.

slope of the best representative straight line. Clearly, the value of G should be independent of a, which, being known, enables G to be calculated. The resulting curves of G against a are shown in Figure 296*a*. It appears as though G might consist of two parts, a constant term G_0 and a term X that is a function of the scanned area a, or

$$G^2 = G_0^2 + X^2a. \tag{4}$$

This matter will be discussed below.

In Selwyn's first paper, he had derived an expression for the probability that a chosen area has a density lying within the range $\Delta \pm d\Delta/2$, the average density being D, on the basis that the deposit consists of grains of equal linear dimension c distributed at random. Although experimental counts on various types of particle confirmed the assumption of random distribution, the theory did not lead to a useful expression for granularity. It did, however, indicate that the variation of granularity with grain *diameter* should be

$$G/c = \sqrt{0.87D[1 - f(D)/D_\infty]}.$$

Photomicrographs of the grains in the six emulsion
made and the mean grain sizes determined. T
ranged from 0.79 μ to 2.20 μ, were only slig
density of the deposit. When G_0/c was
fairly representative curve was found

$$G_0/c = \sqrt{}$$

The data, however, were t
indication of the validity o

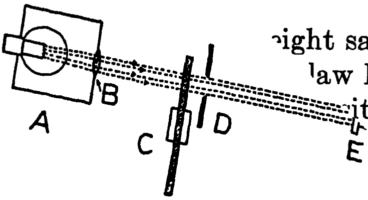
Selwyn plotted the distribution curves for all his emulsions together on Gaussian co-ordinate paper, having reduced all the data to a common basis, and determined the magnitude of the deviations of the individual points. From this study, he concluded that

> ". . . it is probable, therefore, that the density distribution function is not exactly Gaussian. Nevertheless, the variation from Gaussian is small and for practical purposes the distribution function may be taken as Gaussian."

The slight departure from Gaussian is not surprising because, as Fisher,[28] the statistician, emphasizes, most distribution curves representing natural phenomena are skew and are not the symmetrical, one-parameter, Gaussian variety.

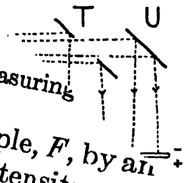
Some years earlier, van Kreveld[29] had plotted the distribution of density deviations as shown by the microdensitometer for numerous emulsions and concluded "that the observations satisfy the Gaussian law fairly well." He noticed a slight positive asymmetry, which he attributed to dust and scratches, the bane of workers in this field, but felt that this could be disregarded. Having established the applicability of the Gaussian law, he then inted out an interesting property of it. Image a template ining two parallel slits, separated by interval i, to travel he axis of the microdensitometer trace, the slits being this axis. Through one slit, the deviation of the trace n at any instant is Δ_1; through the other, it is Δ_2; s $\Delta_1 - \Delta_2$. After the template traverses the enc mine the mean value m of the instantaneous small distribution is Gaussian and the mean devia- effect. Th Figure 297.

$$[illegible] = \Delta_m\sqrt{2}. \tag{7}$$



ight samples, using 400 differ- law held well unless i was so itometer slit produced an was made as shown in es the diaphragm, D,

FIG. 297. van Kreveld instrument for measuring



through a lens, B. D is focused on the sample, F, by an E; C is a neutral wedge to control the intensity of the After traversing the sample, the light is focused on two pho cells, H_1 and H_2, by an objective, G. The beam destined for H_1 is reflected at the annular mirror, T, while that for H_2 is reflected at the circular mirror, U. No trace is made; instead, the cells are connected to oppose each other, and the resulting differential current is rectified and fed to a highly damped galvanometer of long period (twenty seconds in van Kreveld's apparatus). As the sample, F, is moved in its own plane, the constantly varying density difference causes the galvanometer to deflect from its zero position; but it remains fairly steady and indicates a mean value by virtue of its long period and high damping. Thus, the granularity of the sample is given immediately by the scale reading.

van Kreveld[30] then refined his results. He derived a formula for eliminating the effect of the sluggishness of the short-period galvanometer used in his electro-optical rectifier. Then he made runs with differently sized diaphragms and obtained results of which those for the following samples are shown in Figure 296*b*:

A_1 Ilford Special Rapid	Density = 0.35
A_2 Ilford Special Rapid	Density = 1.00
B_1 Gevaert Contrast	Density = 0.27
B_2 Gevaert Contrast	Density = 0.88
C_1 Gevaert Supercontrast	Density = 0.35
C_2 Gevaert Supercontrast	Density = 1.08

On the whole, the measured granularity is independent of area; but if the galvanometer correction is not made, the general trend is upward, as shown by Figure 296*c*. An upward trend is also manifested by Selwyn's results, shown in Figure 296*a*, and, with a good deal of uncertainty, by some data obtained on one emulsion by Hansen and Keck,[22] which are plotted in Figure 296*d*. Here the ordinates represent mean deviation of transparency ΔT times scanning-beam diameter.

The reason for the rise of granularity with diameter of beam is not clear. One possibility, suggested by Selwyn, is that a long-period pattern is superposed upon the short-period deviations, the long-period pattern increasing in magnitude with area. Some support for this can be obtained from the microdensitometer traces.

A more general approach is made by Goetz and Gould,[31] who blacken the record on one side of the microdensitometer trace. This record is then placed in the integrator sketched in Figure 298. R is the record which is illuminated by the lamps L. The lens, O, forms an image of the record on the photocell, C, associated with the galvanometer, G_2. Tube T shields the lens from extraneous light. A template, S, with a lengthwise slit moves transversely across the record and, as it does so, the galvanometer swings from its position for a completely opaque record to that for a completely clear record. The plot of deflection against the displacement of the template clearly represents the distribution of density deviation represented by the trace.

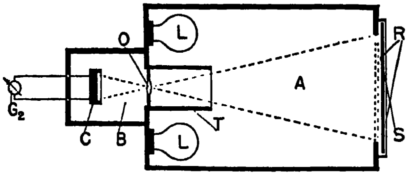


Fig. 298. Simple Goetz-Gould trace evaluator for measuring granularity.

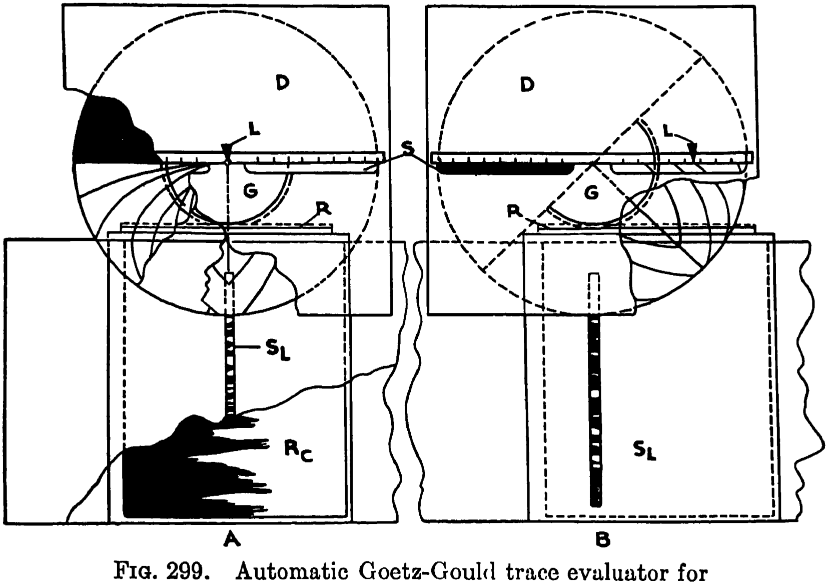


Fig. 299. Automatic Goetz-Gould trace evaluator for measuring granularity.

To avoid the labor of plotting and then evaluating the curve, Goetz and Gould propose the device sketched in Figure 299. The record, R_C, moves horizontally behind a slit, S_L. As it does so, a rack, R, rotates a disk, D, by means of a gear wheel, G, and the galvanometer spot, L, moves sidewise along the slit, S, in the mask covering the disk. This disk has a family of curves drawn on it, as shown in Figure 300; and if the distribution of density deviation follows the law assumed when drawing the curves, the galvanometer spot will follow one curve from beginning to end as the sample is moved. Since each curve is characterized by a particular value of the parameter representing granularity, the granularity of the sample is indicated by the curve selected by the galvanometer.

The law assumed by Goetz and Gould had the general form

$$P(\Delta T, \Delta T + dT) = \frac{C}{G} e^{-(\Delta T/T_m G)^n}. \qquad (8)$$

Here, $P(\Delta T, \Delta T + dT)$ is the probability that a deviation in transparency (their microdensitometer values were read in transparency units because photocell current is linear with respect to incident flux) from the mean lies between the value ΔT and $\Delta T + dT$, C is a constant, G is the granularity constant that determines "the rate of decline of the occurrence of relative amplitudes of the fluctuations ΔT," and n is a constant which determines the nature of the function and which is assumed to have a value of from unity to two. If $n = 1$, the expression is a simple exponential; if $n = 2$, the expression becomes the familiar Gaussian error function. As a result of numerous trials, the investigators concluded that "the distribution function of the transmittance fluctuations is predominantly a Gaussian probability function upon which a simple exponential distribution function is superimposed." In other words, the function is

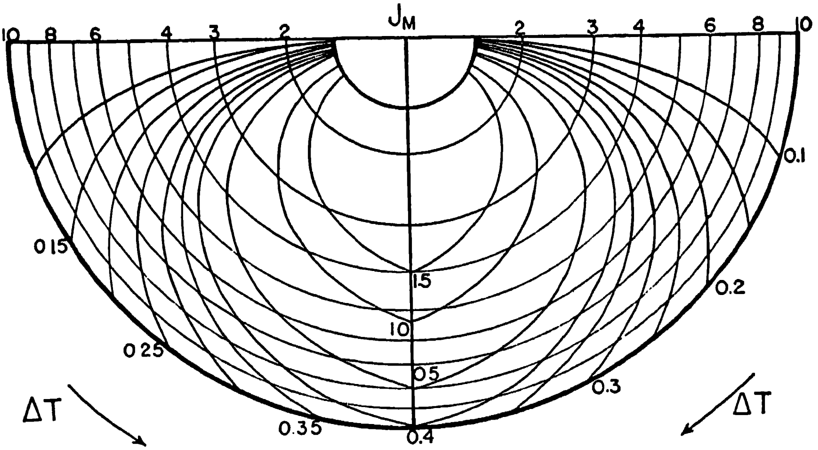


Fig. 300. Plan of disk for Goetz-Gould trace evaluator with family of curves plotted according to assumed distribution laws. Each curve corresponds to a different granularity parameter.

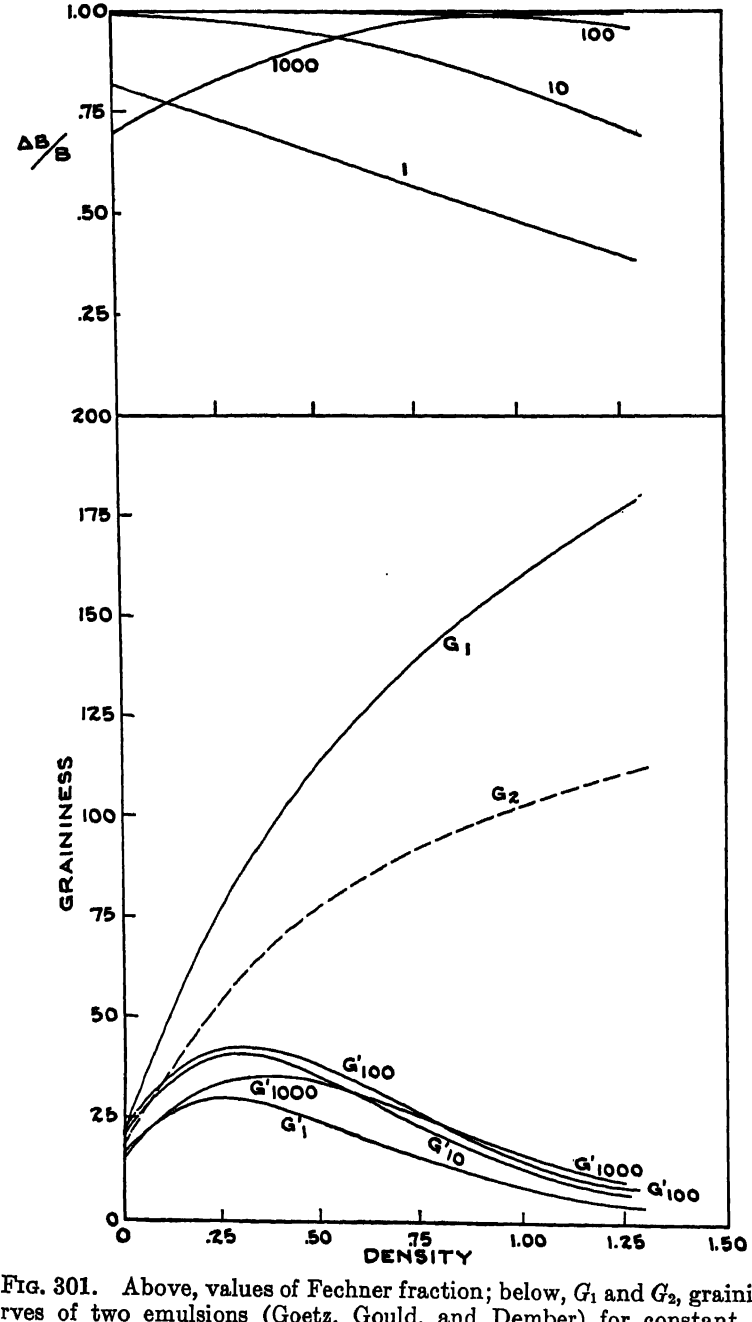


FIG. 301. Above, values of Fechner fraction; below, G_1 and G_2, graininess curves of two emulsions (Goetz, Gould, and Dember) for constant field brightness. Curves labeled G' are computed for constant sample illumination when the field brightness with sample removed has the specified values in millilamberts.

determined by more than one parameter, which is the case for the skew distribution functions usually found in nature.

Certain of Goetz, Gould and Dember's[33] results are reproduced as curves G_1 and G_2 in Figure 301. These compare with Lowry's curves in Figure 291; it is seen that they droop slightly, whereas Lowry's curves are straight. Such an evaluation of graininess is based on *relative* transparency; to make it correspond with constant illumination, it must be evaluated on a basis of *absolute* transparency, which means that the curves must be multiplied by the mean transparency $T_m = 10^{-D}$. But even this is not sufficient, because the contrast sensitivity of the eye varies with field brightness. The topmost curves in Figure 301 show how the contrast sensitivity varies when the field brightness is reduced in terms of the values of density indicated by the abscissas; the field brightness at zero density in millilamberts is given on each.[32] When G_1 is multiplied by 10^{-D} and then by $\Delta B/B$, the curves for G' in the lower part of the figure result.[33] It is seen that they are roughly similar to the curves of Figure 290 although sufficiently different to indicate that some other influence is also effective. One possibility is that, instead of the contrast function of the eye, $\Delta B/B$, the resolving power or the acuity should be introduced into the calculation. The curve for 1000 millilamberts is anomalous in the sense of being low for low densities because of glare at such a high brightness level, but as yet this curve is of more academic than practical interest.

Some correlative work on the basis of mean deviation has been published by Hansen and Keck (*loc. cit.*). They argue that the visual merging of the elements of the granular structure of a photographic deposit when viewed by an observer results in a pattern characterized by a certain apparent mean deviation in transparency over its area. As the observer retreats from the sample, the pattern becomes coarser and its apparent transparency deviation less until, at the blending distance, the deviation drops to the minimum value that can be perceived visually. Presumably, this quantity, ΔT_0, would be constant for all samples.

By the objective method, a scanning beam having a certain cross-sectional diameter d at the plate produces a trace that can be evaluated in terms of mean transparency deviation, ΔT. Moreover, from what has been said a few pages previously, it is permissible to specify for every sample a *sample constant* defined by

$$K = \Delta T \cdot d. \tag{9}$$

For the critical value of transparency deviation, ΔT_0, defined above, this corresponds to a certain diameter of scanning beam, d', defined by the relation

$$K = \Delta T_0 \cdot d'. \tag{10}$$

Returning now to the subjective method, if one observes samples from such distances that the values of d' corresponding to each subtend the same angle at the eye, the limits of enlargement are directly proportional to the viewing distances. Let d_0 be the value of d' for a hypothetical standard sample whose limit of enlargement is unity. The limit of enlargement of any other sample is then

$$M = d_0/d'. \tag{11}$$

The constant of the standard is

$$K_0 = \Delta T_0 \cdot d_0. \tag{12}$$

The limit of enlargement for any other sample can therefore be computed from the relation

$$M = K_0/K. \tag{13}$$

Since both d_0 and ΔT_0 are defined in subjective terms, K_0 is a *physiological constant* against which each sample constant K can be compared to determine the upper limit of enlargement.

Hansen and Keck tested these conclusions by first determining the limit of enlargement in a manner similar to Jones and Deisch's. Then they ran the samples through a microdensitometer and computed the values of the constant K from equation (9). The experimental values thus found are shown in columns 2 and 3 of Table LXXXIV.* From equation (13) the average value of K_0 was found to be 0.21, on which basis the calculated values of M would be those in column 4. The similarity of these values to those in column 2 is manifest. On the assumption that the resolving power of the eye is 1′ of arc, Hansen and Keck computed that $d_0 = 0.072$, in which case the value of ΔT_0 determined from equation (12) for each sample would be as given in column 5. It is evident that the values are practically constant, indicating that the eye does indeed set a constant transparency deviation as its criterion of just perceptible graininess.

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* The limits of enlargement in column 2 are probably lower than would be permissible in practice, as Hansen and Keck point out, because the presence of details in a photograph tends to conceal the graininess.

TABLE LXXXIV

Observed and Calculated Granularities

Emulsion	*1* $D_\#$	*2* $M_{\text{obs.}}$	*3* K	*4* $M_{\text{calc.}}$	*5* ΔT_0
Agfa Ultra Special	0.48	2.8	0.771	2.8	3.0
Perutz Silbereosin	.54	3.0	.735	2.8	3.1
Perutz Persenso	.24	3.0	.671	3.1	2.8
Hauff Ultra	.22	3.6	.614	3.4	3.1
Perutz Perorto	.21	4.2	.531	3.9	3.1
Perutz Silbereosin	.23	4.3	.444	4.7	2.7
Agfa Diapositiv	.40	6.3	.342	6.0	3.0
Perutz Reproduktion	.20	7.0	.275	7.5	2.7

The general conclusions regarding graininess found by various investigators may be summarized as follows. First, as to the negative itself:

1. The relation of graininess to density for constant illumination (or constant exposure in a photomicrographic camera) is as shown in Figures 288 and 290.
2. The relation for constant field brightness (or constant density of a photomicrograph) is as shown in Figure 291.
3. The conditions under which fixing, washing, and drying are conducted have no effect upon graininess. Hardy and Jones found that this was the case provided reticulation was avoided and the effect of density variation was eliminated.
4. Granularity increases with development time, as several investigators have found. Some unpublished data obtained in the Kodak Research Laboratories indicate that a long development time and low exposure produce more graininess for a given density than do the opposite set of conditions. It should be noted, however, that γ also increases with development time, and van Kreveld found that the ratio of granularity to γ is essentially constant. It might therefore be expected that the development of the negative would not change the graininess of

the positive since an increase in the granularity of the negative with longer development would be balanced by the advantage obtained from the use of a softer paper for printing.

5. Most developers give practically the same graininess provided density and γ are held constant. For a discussion of the means which may be employed to diminish graininess in development, see Chapter XI, p. 461.

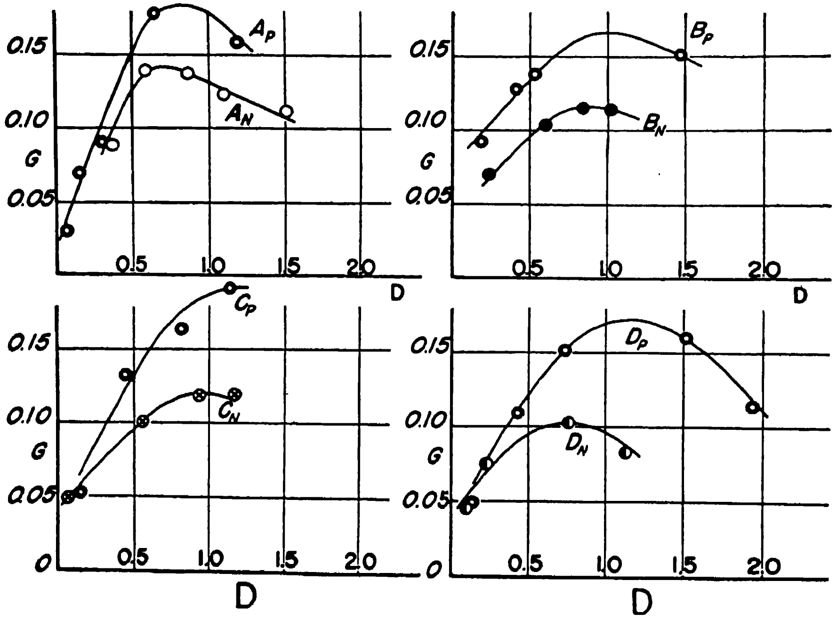

FIG. 302. Granularity-density curves of four negative emulsions and of prints made from them measured on the Goetz-Gould trace evaluator. A single positive material at a constant exposure was used.

6. Crabtree[34] points out that storing an exposed film in warm, damp air not only accelerates the fading of the latent image but also increases graininess.

But the negative is only a means to an end, so it is essential to consider the graininess of the positive made from the negative.

1. Figure 302, from Goetz and Gould, shows the granularity of four emulsions, A_N, B_N, C_N, and D_N, as well as the granularity of prints made from them on positive film developed to a γ of 2.1. The granularity of a positive is greater than that of the corresponding negative of the same density because of the

superposition of the pattern of the negative film on that of the positive.

2. The granularity of a positive may be compared with that of the negative from which it was made; if the negative is thin, the positive will be dense, and vice versa. If the "printing factor" $P = G_P/G_N$, the relation of P to D_P is shown in Figure 303, which is from the same data as Figure 302. For a given

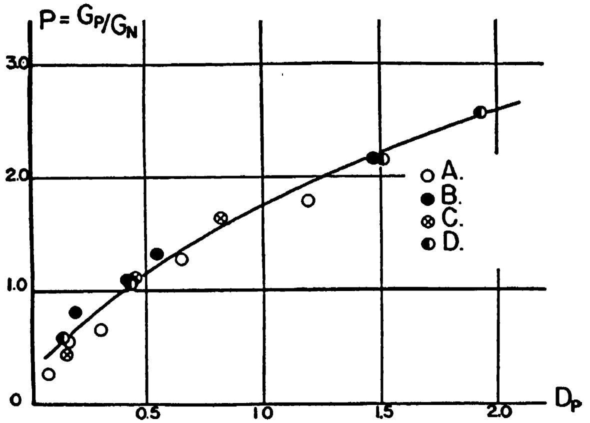

FIG. 303. Ratio of the granularity of a positive to that of the negative from which it was made as a function of the density of the positive. The symbols correspond to those of Figure 302.

D_P and γ_P, the value of P is independent of G_N. However, G_P is proportional to G_N under these conditions. G_P is greater than G_N unless D_P is below approximately 0.4.

3. The time of development of the negative should have no effect on the graininess of the positive provided the γ-product and the positive density are constant, as deduced in (4) above. Hardy and Jones show that this is so by the data plotted in Figure 304, and Crabtree confirms this result. Nevertheless, all workers are not convinced as to the sufficiency of the evidence.

4. The density level of the negative has a profound effect. A thin negative and a dense one can be printed to give positives that are identical in their gross characteristics by adjusting the printing time. Their graininess characteristics, however, will be very different, as Figure 305 shows. Here the graininess of the positive is plotted as a function of its density for negatives that increase in density level from A to E. Evidently, the

negative exposure should be kept as short as tone reproduction will permit.

5. The effect of graininess in a picture is influenced by both density and the presence of details. For example, a large, uniform area of density around 0.4, such as a wall or the sky, is especially likely to show graininess.

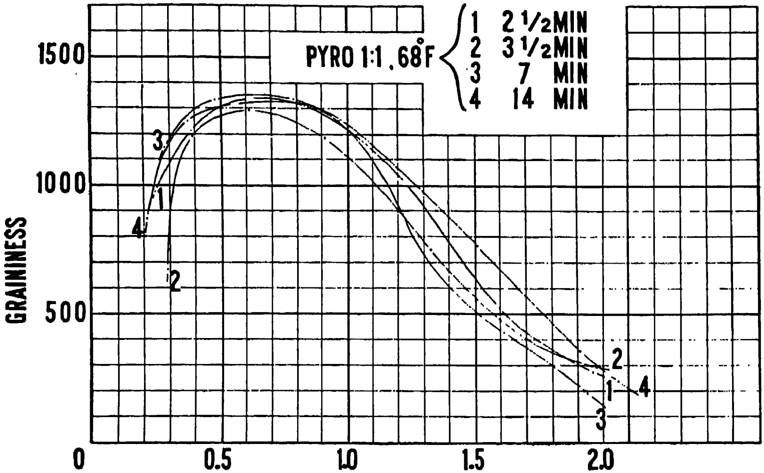

Fig. 304. Graininess-density curves of matched prints. The development times refer to the negatives.

6. Diffusion of the incident light in printing is conducive to low graininess. In the case of contact printing in an ordinary printer, any reduction in graininess is at the expense of definition, according to Hardy and Jones.

The situation with respect to motion pictures differs from that for still pictures because the grain patterns of the successive images do not coincide. No systematic investigation under conditions in which successive images are viewed seems to have been published at the present writing. In sound recording, the granularity of the emulsion is evidenced as ground noise, and the useful power range is the maximum undistorted output less the noise power. Albersheim[35] investigated the matter by regarding the illuminated area as a mosaic of black grains and clear gaps, and on probability considerations deduced two expressions for the probable deviation ΔT of the transparency of the deposit:

Let the area of the scanning beam be a, the grain area be a', and the mean transparency and density be T and D, respectively. Then, if the image is confined to the surface,

$$\Delta T = 0.675T\sqrt{\frac{a'}{a}}\sqrt{\frac{1-T}{T}}. \tag{14}$$

If the image extends into the emulsion,

$$\Delta T = 1.022\sqrt{\frac{a'}{a}}\sqrt{D}. \tag{15}$$

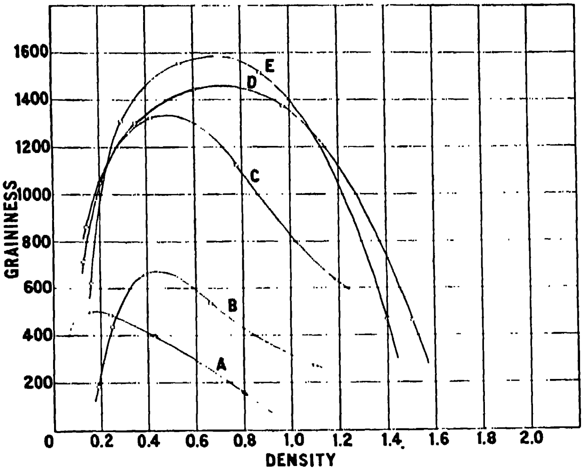

FIG. 305. Graininess of the positive as a function of the density of the negative measured on the Jones-Deisch instrument. The density level of the negative increases from A to E, but that of the positive was held constant by adjusting the printing exposure.

In either case, the amplitude of the ground noise varies as the square root of the area of the individual silver grains. Moreover, it varies inversely as the square root of the scanned area, as was shown previously. No help in reducing noise is derivable from this source, however, because the length of the slit is fixed by the width of the track, while its width cannot be increased because the frequency range would be proportionately reduced. If the volume range is computed for the two cases, the results shown in Figure 306 are obtained for variable-density recording. Unfortunately, the usual density is approximately 0.7, so the peaks of the curves cannot be utilized. Sometimes, ultraviolet light is used in recording to confine the image to the surface and thus reduce the spreading occasioned by turbidity. Although the attenuation at high frequencies is thus reduced, the figure shows that the volume range is correspondingly lowered.

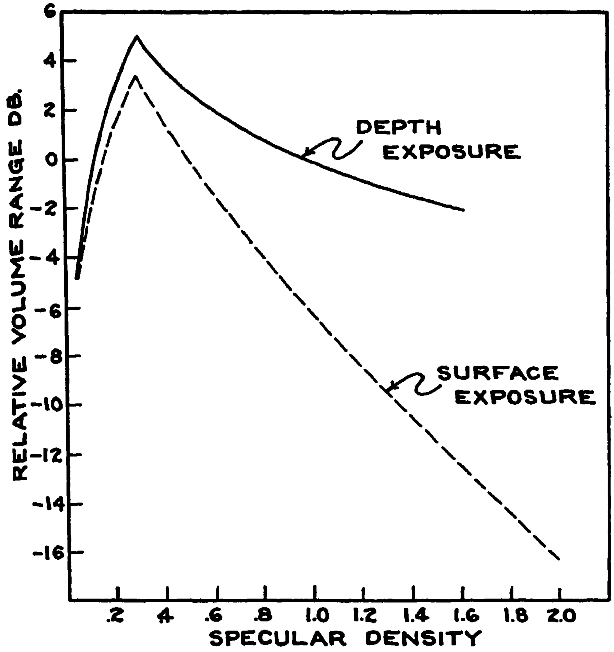

Fig. 306. Computed volume range of a sound record as a function of exposure (Albersheim).

Albersheim also derived an expression for the relation between noise level and specular density. As Figure 307 shows, it fitted the data of at least one experiment.

Until the problem has received more study, it may be assumed that the methods of measuring granularity which have been worked out for picture photography can be used for sound recording. In the case of variable-area recording, a sample of uniform density is hardly suitable because the chief effect is produced by the errant grains at the boundary between the dense and the clear areas. The procedure followed in the Kodak Research Laboratories is to make a knife-edge image, as described in the next section, and run this across the slit of a microdensitometer, the slit being normal to the edge of the image. The amount of slit that is covered by the dense region is not important, but as little as possible should be covered by the clear region because, otherwise, the fog grains will mask the edge granularity. The resulting trace can then be measured by inspection or by some mechanical device, as previously described.

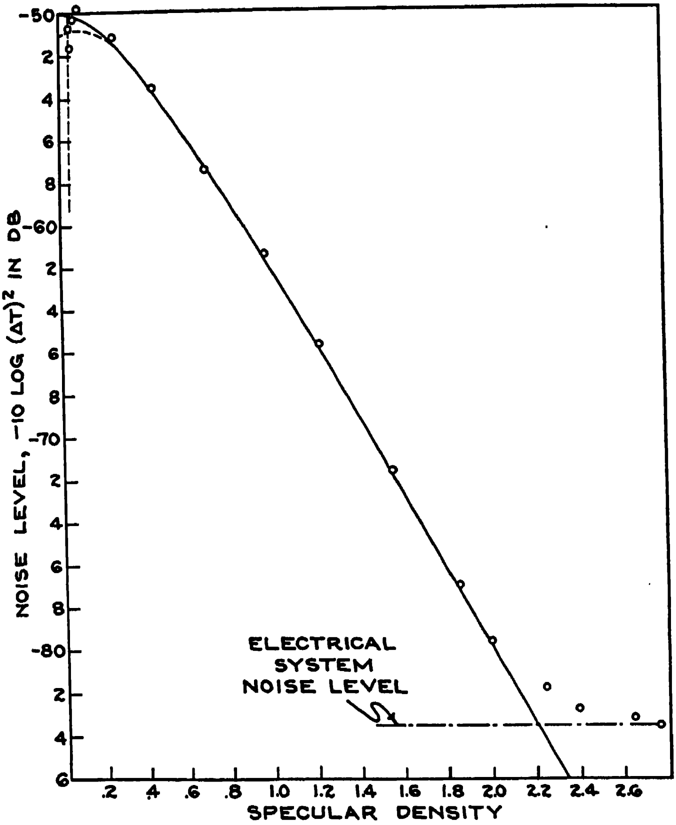

Fig. 307. Ground noise of a sound record as a function of density (Albersheim). The curve is computed from theoretical considerations; the points represent experimental values for a certain positive emulsion.

TURBIDITY, SHARPNESS, AND THE EBERHARD EFFECT

If a photographic plate is exposed to light while partially covered by a shield having a knife edge in contact with the plate, the developed image does not end abruptly at the knife edge; by reason of diffusion* resulting from refraction, reflection, diffraction, and scattering at the silver halide grains, the image encroaches upon the shaded area and has a diffuse boundary.* Consider the image of a slit bounded by parallel knife edges in contact with the emulsion: Neglecting the diffuseness of the edges, the image in general is wider than the slit, and this widening may be considered to indicate the turbidity of the emulsion. A rough quantitative measure can be obtained by photographing a slit on a microscopic scale by reduction in a camera, an optical wedge being placed against the slit to attenuate the light logarithmically from one end to the other.[36] Photomicrographs of the resulting images made on three modern emulsions are shown in Figure 308. Diffraction and Rayleigh fourth-power scattering should be chiefly responsible for the diffusion in the case of fine-grain emulsions, and these phenomena increase with decreasing wave length. For coarse-grain emulsions, reflection and refraction should predominate, and these are practically independent of wave length. Experiments with red and blue filters (*loc. cit.*) indicated that these types of diffusion are, indeed, associated with these respective types of emulsion. Confirmation was given by microscopic examination of the images. The diffraction type of diffusion should increase from the front to the back of the emulsion, and this increase was found in the case of fine-grain plates. The diffusion in coarse-grain plates, however, was found to be independent of depth.

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* The terms *scattering* and *irradiation* are frequently used to denote this phenomenon, but these terms have other specific meanings, whereas *diffusion* has not acquired any other definite connotation as applied to light and is, therefore, less ambiguous.

The diffusion of the image depends not only on the optical turbidity but also on the opacity of the emulsion. In a wet-collodion plate, the optical turbidity is high; but the opacity for the actinic light is also high, so the light diffused sidewise is rapidly absorbed and the developed image is kept within narrow bounds. The photographic turbidity is therefore low although the optical turbidity is high; to avoid confusion, the unqualified term *turbidity* is used solely to mean *photographic turbidity.* Exactly the opposite condition obtains in the case of a Lippmann emulsion, which is practically grainless when properly prepared. It is so translucent that both diffusion and opacity are low, so the turbidity is also low. The optical turbidity of such an emulsion can readily be increased by heat, aging, or other ways, in

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* The phenomenon of halation, which arises from reflection at the back surface of the emulsion support, is being neglected since it is not a characteristic of the emulsion and can be eliminated by backing the support in the well-known manner.

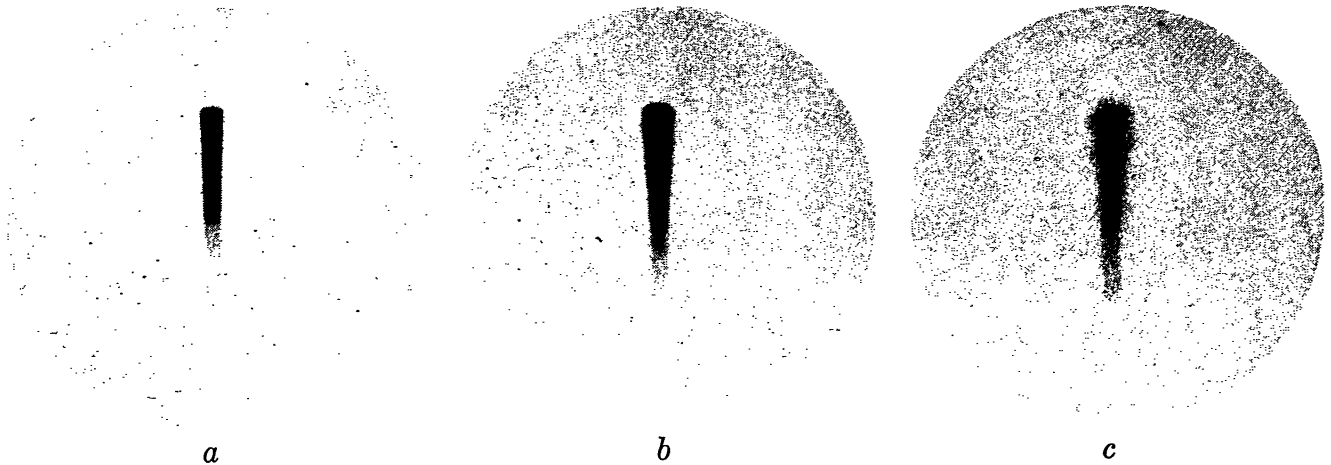


FIG. 308. Photomicrographs (×43) of the image of a slit covered by an optical wedge on (a) Microfile film, (b) process film, and (c) portrait film.

which case the photographic turbidity may become high and the resolving power correspondingly low.

Most turbidity investigations have been made to determine the effects of the phenomenon and not its cause, and so general laws of light absorption have been assumed rather than special laws based upon specific mechanisms. One important point requiring study is the effective law of absorption. If Beer's law held, as it does for homogeneous materials, the density of the silver halide layer would be

$$D = aW^1, \tag{16}$$

where W is the concentration of silver halide. Bloch and Renwick[37] found, however, that the exponent is not unity but that, for white light,

$$D = 0.66W^{0.64}. \tag{17}$$

According to this, the absorption is greater in the upper layers and less in the lower layers than it would be if Beer's law held. In Figure 309 are shown equiluminous surfaces A . . . N in an emulsion calculated by Bloch and Renwick's equation. Each surface represents an additional 10 per cent absorption, but the surfaces are not equidistant, as they would be on the basis of Beer's law.

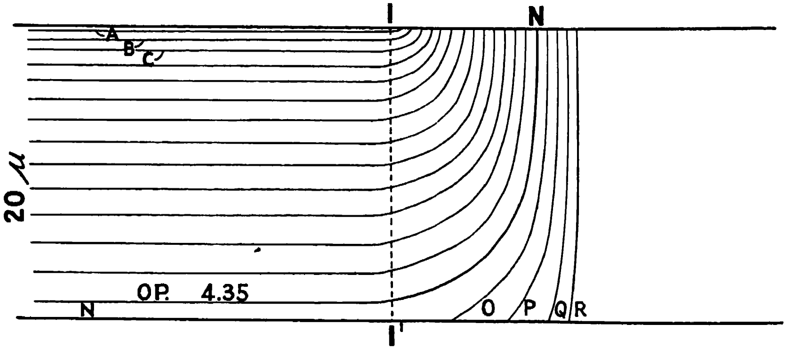


FIG. 309. Equiluminous surfaces in an emulsion at the edge I–I′ of an image.

Before considering the law governing the light distribution within the shadow, the edge of which is at I–I′, the distribution of light just inside the image should be studied. Obviously, the light scattered outside must entail a deficiency inside, and the figure with its parallel equiluminous surfaces extending to the edge I–I′ cannot accurately represent the situation. The law of diminution is not known, however; and, indeed, some experimental evidence indicates no diminution whatever. Thus, Figure 310*a*, which shows magnified sections of a sharp slit image, shows the silver deposit ending abruptly at the edges. This proves nothing about the *light* distribution, however, because the development conditions at the edge of an image are quite different from those at the center.

The effect of distribution of density in an image upon the development of specific areas of that image was studied by Eberhard,[38] who exposed photographic plates behind a screen in which were circular openings of varying diameter from 0.3 millimeter to 30 millimeters. He found that the densities of the developed plate were not uniform but that the smaller images were denser than the larger, as if the smallest had received from one and a half times to twice as much exposure as the largest. This local variation in density is now known as the *Eberhard effect* and is a particular type of what are often referred to as *neighborhood effects* (*Nachbareffekt*). Eberhard found that all kinds of plates gave effects of the same order but that the amount of the effect increases with the thickness of the coating. The effect grows with exposure but is greatly diminished by an exposure of the background or by the development of fog. All the organic developers studied were found to give the effect to an extent dependent upon the concentration, being greatest for weak developers. During the course of development, the effect rises to a maximum and then decreases as development is continued. All these results were held by Eberhard to point to an origin of the effect in the accumulation of development products during development which tend to slow down the growth of the image. With very small images, this production of oxidation products and soluble bromide is low; the developer retains its original strength and produces greater density than for larger areas, where the developer is converted to its oxidation products to a greater extent. Eberhard concluded that the effect would not be shown by a ferrous oxalate developer, and he found experimentally that such was, indeed, the case. For this reason, he

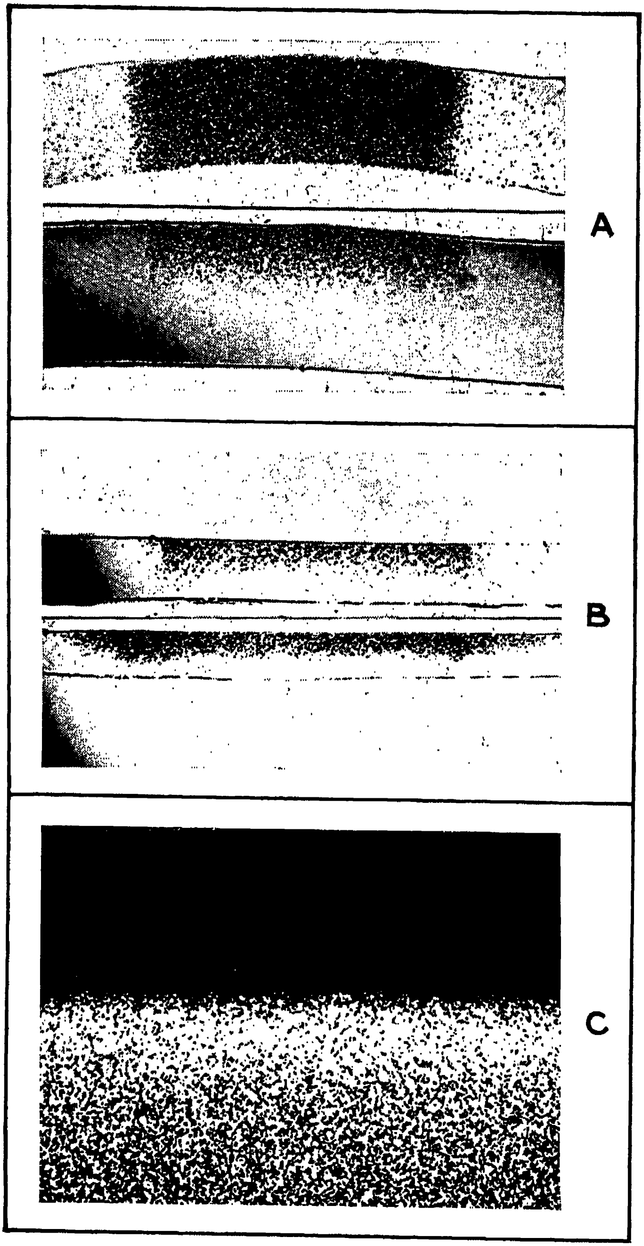


Fig. 310. Photomicrographs showing edge effects: *A*, cross sections of uniform density; *B*, cross sections of greater density at boundaries (Eberhard effect); *C*, Mackie line outside image.

advocated the use of ferrous oxalate developer in scientific work. Furthermore, he pointed out that the Kostinsky effect (p. 910) may also be considered to be one type of neighborhood effect.

A very complete experimental study of the Eberhard effect was made by Valenkoff,[39] who studied the problem by making microdensitometer traces across the exposed areas. A typical trace is shown in Figure 311. It is seen that the density is appreciably higher at the edges than at the center of this image. Valenkoff specified the amount of the neighborhood effect in terms of $\delta_D = D_{\text{max.}} - D_{\text{min.}}$. He found it to increase with the grain size of the emulsion, so that very fine-grain plates show no effect, while in coarser-grain plates the effect may be as much as 7 per cent of the density. No effect was found when the images were produced by X-ray exposures, and ferrous oxalate was not found to give results differing in any way from the organic developers.

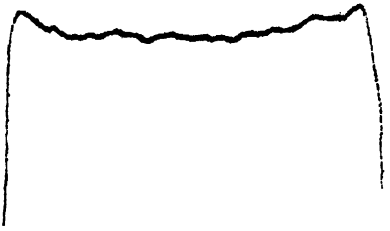


FIG. 311. Microdensitometer trace across a small image showing the Eberhard effect (Valenkoff).

Valenkoff concluded that the effect is essentially one of the border of an image and is greatly dependent upon the sharpness of the image. In large images, it is confined to a region within a millimeter or two of the border, but in smaller images there is apparent an increased density in the middle of the image. The effect is generally small, commensurate with the precision of measurement. For highly sensitive emulsions, however, it may amount to a density difference of as much as 0.10.

Junkes[40] summarized the available information about the influence exerted on the density of any small area of a photographic image by the surrounding densities. He agreed that the effects result from the distribution of substances which affect the process of development. These effects may be either general or only local:

I. If there is a weakening of the developer as a whole by general fog, this may be termed a *fog effect* and becomes apparent by a flattening of the characteristic curve.

II. Local interference with normal development conditions is produced by movements of the products of development both outside the emulsion and within it.

A. Such local movements outside the emulsion give rise to developer and bromide streaks.

1. Developer streaks are relatively dark streaks on uniformly exposed areas, caused by the flow of fresh developer over the photographic emulsion.

2. Bromide streaks are light fringes around areas of great density on fogged plates, and are due to movements of bromide and other reduction products which inhibit development.

B. The movements within the emulsion produce very sharp, dark or light fringes at the border of sharply defined images that have received widely different exposures.

1. Pure phenomena of this type occur at the edges of large areas—*border* and *fringe* effects.

(*a*) The border effect appears as an increase in the density of the margin of a uniformly exposed, sharply defined image, relative to the density within the image itself. It is caused by the diffusion of fresh developer into the exposed image from the neighboring unexposed background.

(*b*) The fringe effect appears as a diminution in the fog density along the boundary of a well-exposed and sharply defined image as a result of the diffusion of reduction products from the image.

2. If the images concerned are sufficiently small, the purely border and fringe effects may overlap.

(*a*) If the images are homogeneous and symmetrical, like a disk, the effects are termed *diameter effects*. For example, consider a small circular image that has received more exposure than the background: The border effects of the opposite edges then overlap and the density at the center is greater than the same exposure would produce on a large area. The smaller the image, the greater is this increase in density. On the other hand, if the image receives less exposure than the background, the fringe effect lowers the density within the image.

(*b*) If the images giving rise to the border or fringe effects are inhomogeneous and unsymmetrical, a Kostinsky effect may occur under certain circumstances. This is a mutual repulsion of the effective centers of density of small adjacent images; since it concerns the movement of an image rather than an alteration in density, it will be treated later (p. 910).

The neighborhood effects are of great importance in motion-picture work, particularly in connection with the duplication of motion pictures. It is common practice in motion-picture photography to print from duplicate negatives, so that the photographic process goes through four stages in producing the finished print: There is, first, the original negative; then, the master positive; then, the duplicate negative; and, finally, the release print. Since the neighborhood effects occur at each stage, they can produce very undesirable distortions of tone rendering in this multiple process. In Figure 312 are shown two characteristic curves obtained upon motion-picture positive film, curve *B* being made from contiguous, exposed areas about a centimeter square and curve *A* from small circles of about $1\frac{1}{2}$ millimeter diameter with relatively large unexposed areas between each step. It is seen that, throughout the upper part of the curve, the small circular dots show appreciably more density than the larger sensitometric areas. The constitution of the developer does not seem to modify this effect very much. The addition

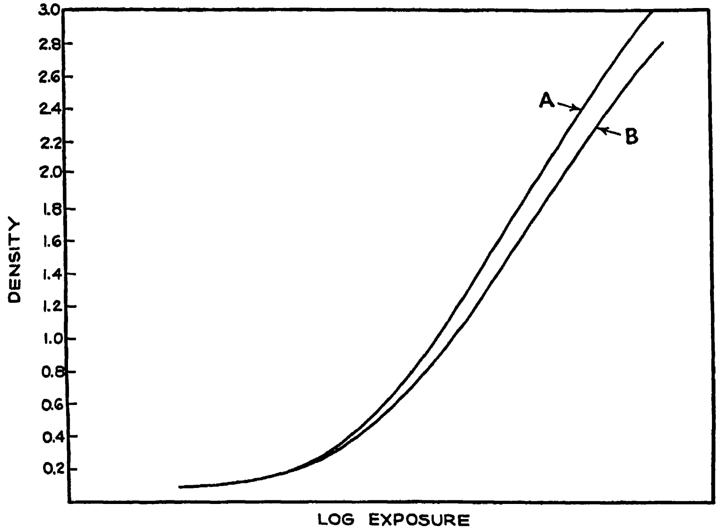


FIG. 312. Characteristic curves for positive film exposed (*A*) in areas of about $1\frac{1}{2}$ mm. diameter and (*B*) in areas of about 10 mm. diameter.

of bromide, for instance, does not lessen it appreciably. The effect is, however, greatest for moderate degrees of development, diminishes when the development is prolonged, and becomes negligible as the development approaches the limit. The effect can, therefore, be greatly diminished by the use of a material which has a low value of γ_∞ and which can, therefore, be developed so that the effect is negligible. Thus, by the use of motion-picture positive emulsion containing a large amount of yellow dye, duplicate negatives can be made in which the Eberhard effect is unimportant.

The fringe effect appears in general photography in what is known as the *Mackie line;* that is, a sharp decrease of density that occurs just outside a dense portion of the image (Fig. 310*C*).

All these local effects, which in extreme cases can produce large streamlike markings upon the developed image, are minimized by effective stirring of the developer over the surface of the material. For motion-picture work especially, the rapid circulation of developer so as to sweep off the products of development as rapidly as they are formed is provided for in all modern equipment. In sensitometric work also, provision must be made to avoid local streaming effects and to minimize the neighborhood effect by the use of adequate agitation during development (see Chapter XVI, p. 625).

Under some conditions, a narrowing of the image is found, and this is sometimes adduced as proof of the deficiency of light just inside the edge. Thus, Figure 313, which is one of several published by Narath,[41] shows that the width of an image on paper is less than the geometrical image when the density is low. This might be accounted for by the shrinkage of the paper, but it is known that a contraction of the image may take place even in the case of films and plates, the reason being a tanning action on the gelatin by the reaction products of development. This matter is discussed in the last section of this chapter; but its effect is shown in Figure 314, which is from a paper by Jones and Sandvik.[42] The contraction varies, among other things, with the type of developer and the diameter of the image; to anticipate, it may be stated that the contraction is proportional to the diameter of the image provided the latter is less than approximately one millimeter, so the only effect within this size range is to decrease the rate of growth and hence the photographic turbidity.

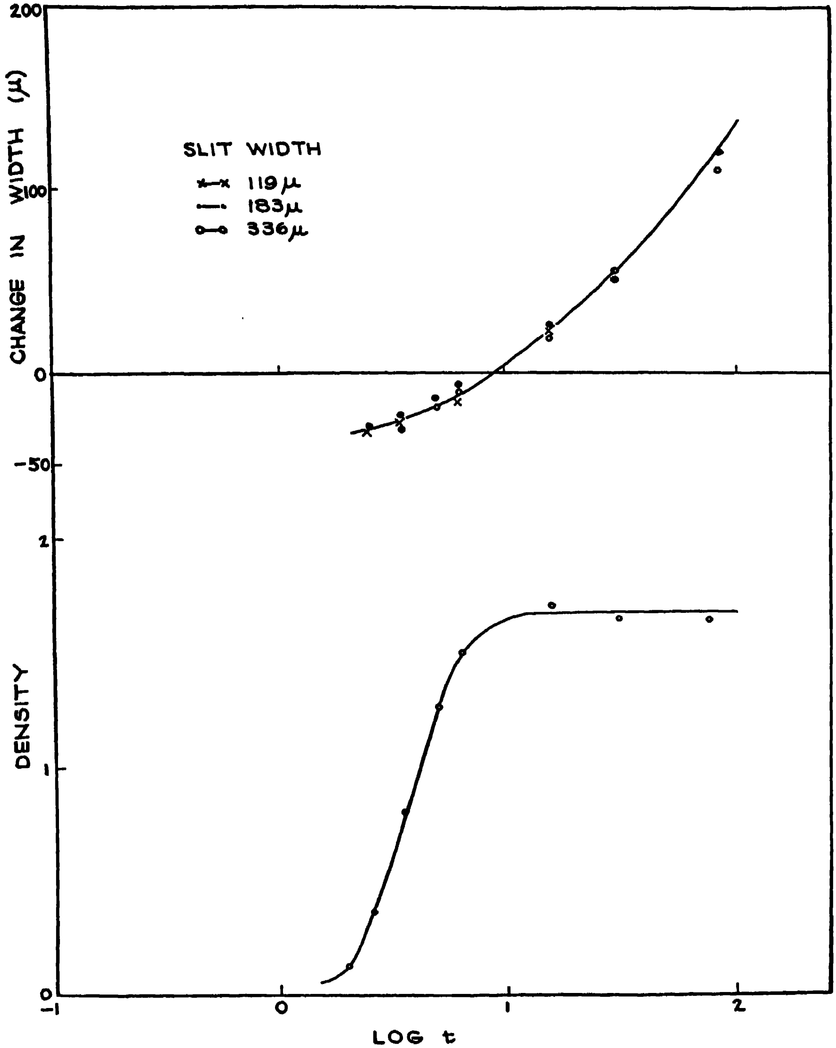


FIG. 313. Change in width of a photographic image on paper with time of exposure, according to Narath. The zero ordinate represents the width of the geometrical image. Below is the characteristic curve of the emulsion.

One of the earliest quantitative investigations of turbidity was made by Goldberg.[43] He exposed plates through a diaphragm pierced with three fine holes placed in contact with the plate. His exposures ranged logarithmically from the threshold value to 10^5 times as great. He found the turbidity of a Lippmann emulsion to be zero for all exposures; for other emulsions, it was zero below an exposure of ten times the threshold and then increased at an accelerated rate. He expressed turbidity as the amount of spreading per unit increase in the logarithm of exposure, or, mathematically, $dx/d \log E$. On this basis, the turbidity of orthodox emulsions at higher exposures increased with the exposure level, varying, of course, from emulsion to emulsion; in other words, $dx/d \log E$ was not constant with exposure. The problem was re-examined by Wildt[44] using monochromatic light; he found the strictly linear relations exhibited by Figure 315. These are for four wave lengths and three diameters of diaphragm. A least-square solution shows that the slopes are independent of the diameter of the diaphragm for any given wave length but that the slope increases with wave length. Wildt explained Goldberg's results by pointing out that the bluer components of Goldberg's heterochromatic light would be more effective on his color-blind emulsions at low exposures than the red, and this would lead to a flattening of his turbidity curve at low exposures. Indeed, Wildt duplicated Goldberg's curves by using a mixture of red and blue light of low intensity. On the other hand, the linear relation has been established in one

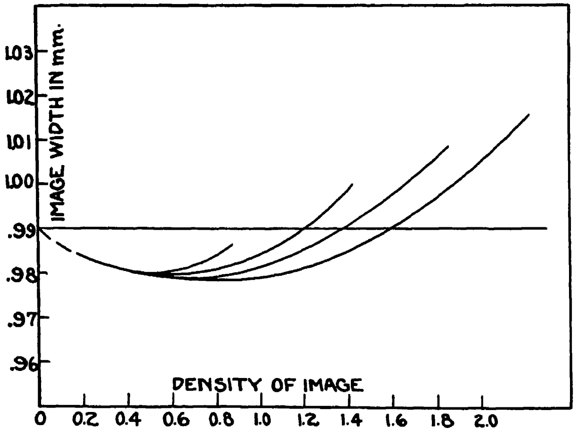


FIG. 314. Variation in image diameter as a function of density for different development times (Jones and Sandvik). The width of the geometrical image was 0.99 mm.

set of experiments for heterochromatic light varying in intensity over a range of five hundred times.[45]

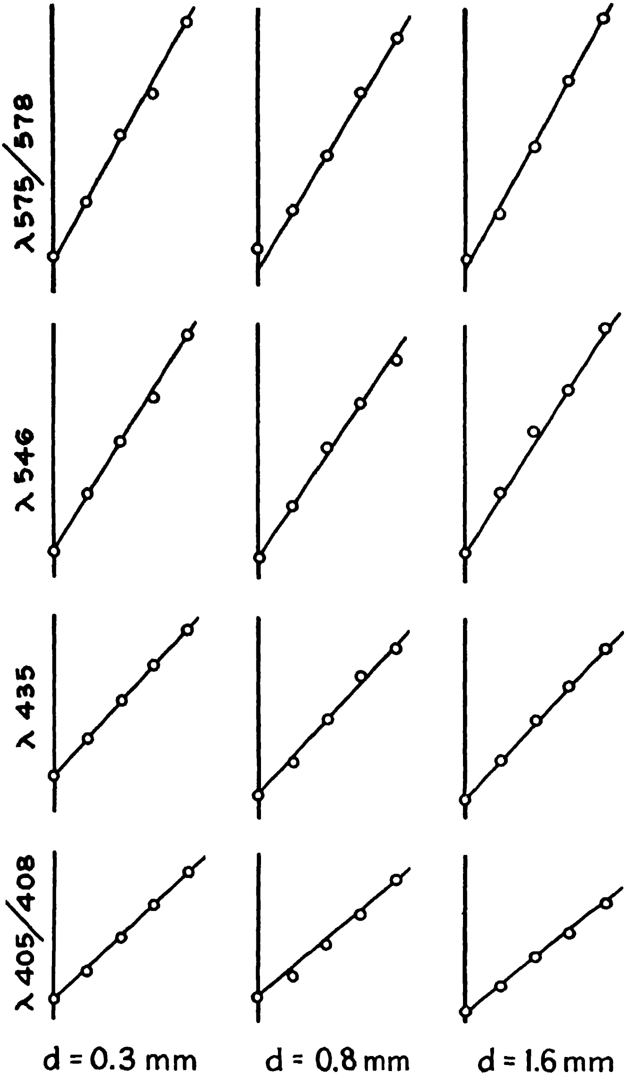


FIG. 315. Variation in image diameter with the logarithm of exposure time (Wildt). Each row represents the wave length of the light used for exposure; and each column, the diameter of the geometrical image.

The phenomenon of turbidity has been utilized in stellar photometry since Bond made the first stellar photograph in 1850.

The straightforward procedure for determining a stellar magnitude would be to measure the density of the photographic image with a microdensitometer and then find the illumination on the plate from the characteristic curve, taking due account of reciprocity failure. Such a procedure is complicated, however, and is subject to numerous sources of error,* so the procedure of measuring the diameters of the images and then deducing the brightness† from the turbidity relation is frequently followed.

From the experiments described above, it might be expected that a satisfactory relation would be

$$d = a + \Gamma \log I, \tag{18}$$

where a and Γ are constants to be determined empirically. Scheiner in 1889 had, indeed, deduced this equation from astronomical observations. By virtue of its analogy to the equation $D = \log i + \gamma \log E$ relating the density of a deposit to the exposure producing it, Ross [47] has proposed that the constant Γ be termed *astrogamma*. The law expressed by this equation is sometimes called the *diameter law* (*Durchmessergesetz*).

Experience showed that Scheiner's formula was not too well followed by astronomical data, and the so-called Greenwich formula came into more general use:

$$\sqrt{d} = a + b \log I. \tag{19}$$

Ross made a series of exposures to artificial stars on a time scale and plotted the diameters of their images according to equations (18) and (19), as shown at A and B, respectively, in Figure 316. It is seen that the Scheiner formula is in error for long exposures, in accordance with Goldberg's results previously discussed; the Greenwich formula is in error for short exposures (or small diameters), which, however, are of little importance in astronomy because stellar disks are rarely smaller than 50 μ in diameter. Ross proposed to modify the Greenwich formula to read

$$\sqrt{d + h} = a + b \log I, \tag{20}$$

---

* Hardly any type of measurement contains so many pitfalls for the unwary as photographic photometry.[46]

† It goes without saying that the illumination in the Airy disk formed by the telescope objective is proportional to the brightness of the star, the size of the disk being determined solely by the size of the objective, except in so far as the "boiling" of the atmosphere tends to enlarge it.

where h is a third constant. Curves C, D, and E represent this formula with increasing values of h; and curve E is, clearly, a quite satisfactory representation of the data. The significance of this investigation is reduced, unfortunately, by the circumstance that the exposures were made on a time scale. When an astronomer compares an unknown image with one of known magnitude on the same plate or another having the same exposure time, he is using an intensity scale. Inasmuch as the exposure range is very great, the reciprocity failure intervenes to prevent a law based upon a time scale from being applied to intensity-scale data without investigation as to its validity under the new conditions.

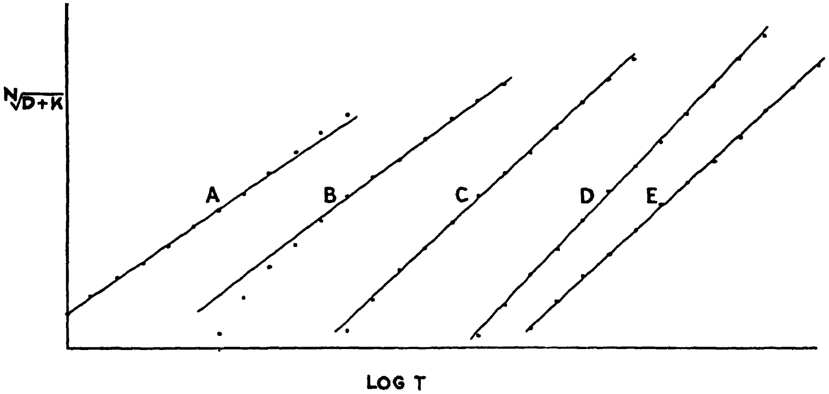


FIG. 316. Plots showing the fit of equations relating the diameter of the image to the time of exposure: A, Scheiner; B, Greenwich; C, D, and E, Ross with increasing values of h.

If the photographic turbidity is assumed to indicate accurately the light distribution within the emulsion, the distribution can be deduced from the turbidity relation. For a homogeneous medium whose light absorption per unit thickness is k, Bouguer's (Chapter V, p. 202) law states that the illumination at a depth x is

$$I = I_0 e^{-kx}, \tag{21}$$

where I_0 is the illumination on the surface. This law may be applied to the sidewise scattering of light from an image. The edge of the image is defined by a certain level of illumination,

$$i = Ie^{-kx} = \text{const.} = a''',$$

where I is the intensity of the incident light and x the distance from the edge of the geometrical image. From this,

$$\ln I - kx = a''$$

and

$$x = a' + 1/k \ln I. \tag{22}$$

If the diameter of the geometrical image is designated by g, the diameter of the photographic image will be

$$\begin{aligned} d &= g + 2x \\ &= a + 2/k \ln I, \end{aligned} \tag{23}$$

which is practically equivalent to Scheiner's formula, equation (18). Since this formula applies in the immediate vicinity of the geometrical image, as curve A in Figure 316 shows, it is reasonable to suppose that Bouguer's law applies there also. The equiluminous surfaces in Figure 309 surrounding the geometrical image were drawn on this basis.

If, instead, it is assumed that

$$i = Ie^{-k\sqrt{x+g/2}}, \tag{24}$$

then

$$\sqrt{d} = a + \sqrt{2}/k \ln I, \tag{25}$$

which is equivalent to the Greenwich formula, equation (19).

In like manner, the assumption that

$$i = Ie^{-k\sqrt{x+g/2+q}} \tag{26}$$

leads to Ross' formula provided q is identified with $h/2$. Figures 317 and 318 show the characteristic differences between these formulas. Near the edge of the image, the Greenwich formula calls for an excessively rapid diminution of flux. On the other hand, Scheiner's law calls for too great a flux density at greater distances. It is true that curve C, in Figure 318, which represents the Greenwich formula, does not appear to match curve B, which represents Ross's formula and, thus, the experimental data; but it does so if its ordinates are multiplied by 5.9. Bloch and Renwick's formula, equation (17), results in a light distribution according to the law

$$k = Ie^{-kx^{0.64}} \tag{27}$$

for white light. This is similar to the Greenwich formula, for which the exponent of x is 0.5, so it may be concluded that the light distribution *at a distance* from the image follows Bloch and Renwick's law rather closely. This law was found to fit the absorption of direct radiation within an emulsion thickness of some 20μ, so, reasoning from analogy, it may be assumed that

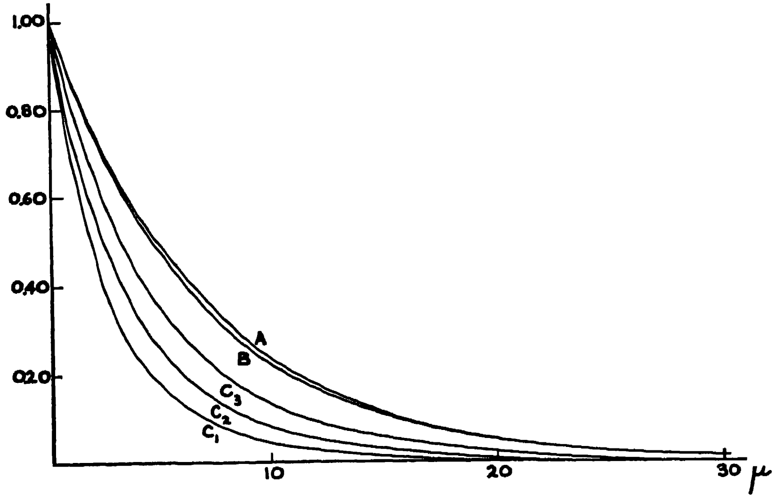


FIG. 317. Light intensity near the edge of an image according to various turbidity formulas: *A*, Scheiner; *B*, Ross; *C*, Greenwich with various values of *g*.

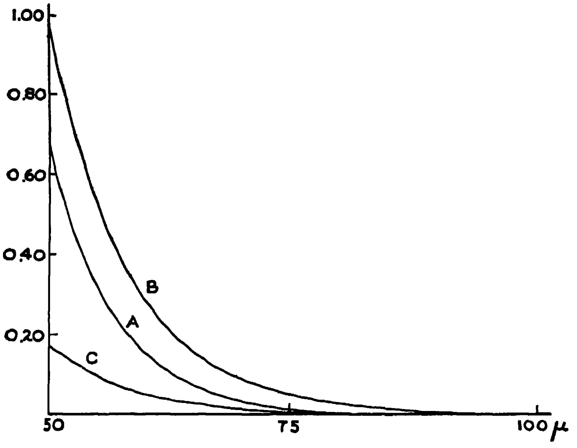


FIG. 318. Light intensity 50–100μ from the edge of an image (continuation of Figure 317).

the law represents the absorption of the direct radiation in the deeper layers, although Bouguer's law is probably a better fit for the topmost layers.

The difficulties in turbidity measurement start with the test object. The simplest procedure would be to photograph a large test object on a microscopic scale according to the technique to be described subsequently in connection with resolving power. This has the drawback that the edge of the image is not sharp, owing to diffraction. Contact test objects that are sufficiently fine have obvious drawbacks. If a circular image is suitable, the technique described by Goldberg [43] can be adopted. He made three dents in a metal plate and then drilled fine holes in the dents; contact with the emulsion surface was assured because three points determine a plane.

The next problem is to measure the images, and the difficulties here can be understood by considering the traces shown in Figure 319, which are for ordinary and fine-grain sound-recording emulsions. If the images are measured visually, each observer will set up his own criterion as to what constitutes the "edge" of the image. The situation is hardly ameliorated by the recording microdensitometer, because some method must be devised for evaluating the traces. The traces of Figure 319 were made on a transparency basis. If the physical evaluation is to be correlated with the visual, it might be preferable to make the traces on a density basis because of the approximately

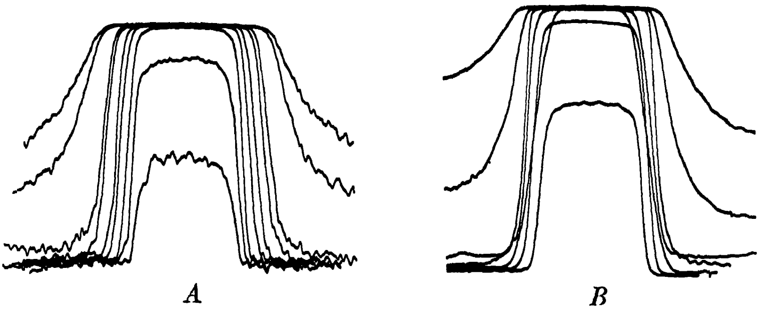


FIG. 319. Microdensitometer traces showing the variation in transparency across the image of a slit as the exposure time is doubled: *A*, ordinary sound film; *B*, fine-grain sound film. The transparency scale is inverted to make a rise in the ordinate correspond to a rise in density.

logarithmic response of the eye. This can be done by means of a logarithmic amplifier.

Various methods of expressing turbidity numerically have been proposed; but, since it is customary to double the exposure of each image, Ross's quantity Δ is perhaps the handiest. This he defined as the increase in width of the image for a doubling of the exposure. It is equal to Goldberg's ratio $dx/d \log E$ when $\log E = 0.3$ and is inversely proportional to the coefficient k in equations (21) to (27). In fact, since from equation (22)

$$x = C + 1/k \ln E,$$

where C is a constant and E is the exposure, then

$$\frac{dx}{d \ln E} = \frac{1}{k} = \frac{0.434\, dx}{d \log E},$$

and, if $d \log E = 0.301$, $dx = \frac{1}{2}\Delta$ by definition, so

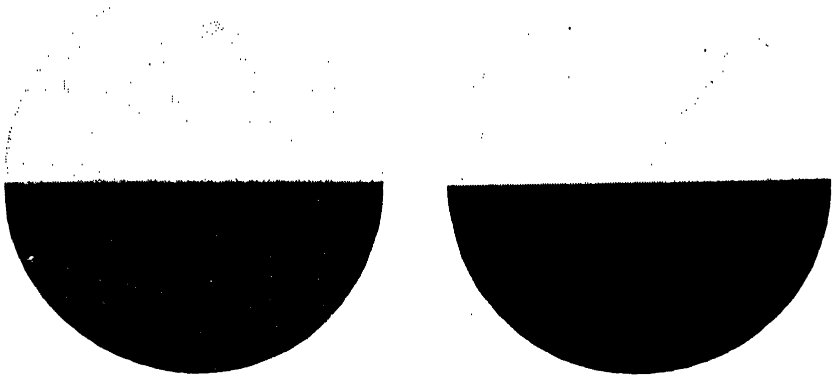
$$\Delta = 1.39/k. \tag{29}$$

Quite a different type of expression has been proposed by van Kreveld,[48] who suggests giving the width of the image between points "where the intensity of the scattered light is half of the incident intensity." This may be a suitable criterion of optical turbidity; but it is hardly indicative of photographic turbidity, because the latter is so difficult to evaluate and, moreover, is so greatly influenced by the conditions of development.

It must be reiterated with emphasis that, in analytical studies of turbidity, the reciprocity failure must constantly be kept in mind. A law based upon time-scale measurements cannot be applied blindly to intensity-scale measurements, especially when the measurements are on the steep portions of the reciprocity curves. The situation is aggravated if one set of measurements is made at high intensity, as is most convenient in the laboratory, and the other at low intensity, as is the case in stellar photometry.

The phenomenon of turbidity becomes important when the widths of lines must be preserved in a photographic copy. In making test objects for resolving-power investigations, for instance, one finds that the lines are widened at the expense of the spaces or vice versa, and the amount of widening is a function of density. The remedy is to use a negative of such a density that the widening of its lines (which correspond to the spaces in the positive) compensates for the widening of the lines of the positive. The proper density can be attained either by controlling the negative exposure or by making a dense negative and then treating it with Farmer's reducer for a suitable length of time.

The knife-edge images made as described earlier have the appearance of Figure 320 when magnified 100 times. These particular images were made on the sound-recording films whose turbidity traces were shown in Figure 319, and the difference in sharpness between the samples is evident. To obtain a numerical evaluation, a graded series of such exposures was made and the images were scanned with a microdensitometer whose slit was parallel to the edge of the image. The resulting traces are shown in Figure 321. The slopes of the straight portions, which represent the transparency variation per unit distance into the shadow where the transparency is approximately 50 per cent (density is 0.3), can then be plotted, as is done in Figure 322. It will be noted that the maximum value occurs approximately at density 1.5 in the present instance; other types of emulsion have their maxima elsewhere.



A *B*

FIG. 320. Photomicrographs of edges of images formed by knife edge in contact with the emulsion: *A*, ordinary sound film; *B*, fine-grain sound film (×68).

As might be expected, sharpness is related to turbidity, although the two phenomena must be clearly differentiated. Sharpness may be defined as the rate of change of density with distance into the shadow, or, mathematically,

$$S = -\frac{dD}{dx}. \qquad (30)$$

If edge effects, such as the Eberhard effect, are assumed to be absent, Goldberg points out that

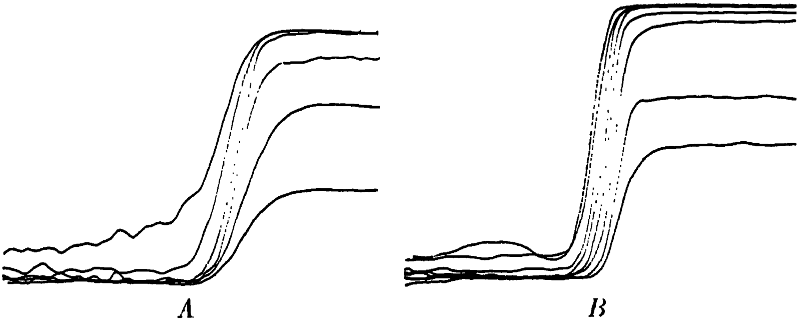


FIG. 321. Microdensitometer traces showing the variation in transparency across knife-edge images on the films of Figure 320. The ratio of successive exposure times is 2 : 1.

$$\frac{dD}{dx} = \frac{dD}{d\log I} \cdot \frac{d\log I}{dx}. \qquad (31)$$

But if the diameter law holds, it can readily be deduced from equation (22) that

$$k = 2.31\frac{d\log I}{dx}. \qquad (32)$$

Also, for the straight portion of the characteristic curve,

$$\gamma = \frac{dD}{d\log I}.$$

Therefore,

$$S = -\frac{k\gamma}{2.31}. \qquad (33)$$

Inasmuch as k is an inverse measure of turbidity, high sharpness and low turbidity go together; and a comparison of Figures

319 and 321 shows that the emulsion with the lower turbidity does, indeed, have the greater sharpness. Increasing the opacity of the emulsion, which has been shown to reduce turbidity, should increase sharpness. Ross[49] has shown that dyeing a plate yellow, which increases its opacity to blue light but not to red, also increases its sharpness for blue light but not for red. Moreover, Sandvik[50] has shown that the sharpness of an ordinary emulsion varies with wave length, according to Figure 323, and the rise at the blue end can be explained by the rise in opacity there.

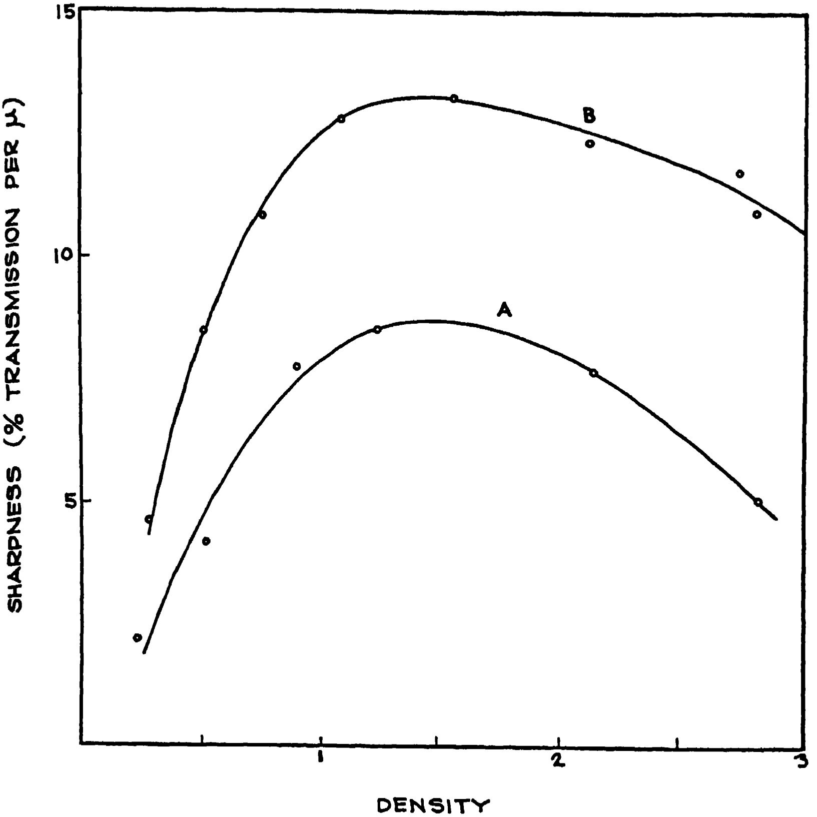


Fig. 322. Variation of sharpness with density as measured from the traces shown in Figure 321: *A*, ordinary sound film; *B*, fine-grain sound film.

From equation (33) it might be concluded that, for equal turbidity, the value of γ would be the only determinant of sharpness. Unfortunately, the formula holds only for the straight part of the characteristic curve; for emulsions with very sweeping toes, the density trails off gradually into the shadow although the sharpness near the geometrical image may

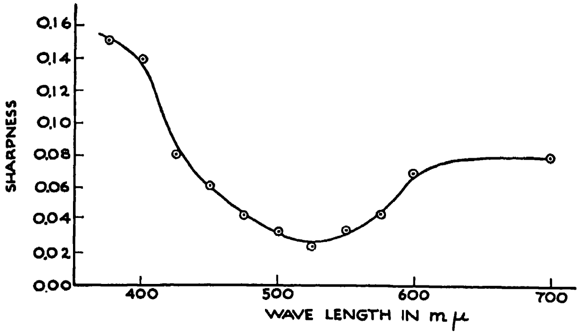


FIG. 323. Sharpness of Eastman 40 plate as a function of wave length. The ordinates are in density variation per micron distance normal to the edge of the image.

be high. Thus, Type *A* in Figure 324 would be superior to Type *B* although the maximum gradient or γ of both is the same. Furthermore, the value of γ in equation (33) cannot safely be taken from the ordinary characteristic curve because the abnormal conditions at the edge prevent the normal density-exposure relation from obtaining there.

Because sharpness is a more complex variable than turbidity and, moreover, is difficult to study without elaborate apparatus, it has received little attention. The obvious method of study is to make traces of knife-edge images in a microdensitometer, as shown in Figure 321. Because of the very great density gradient, a high speed ratio is required between carriage and recording film; for the traces shown, the ratio was 1 : 1600. The image of the slit on the sample must be narrow, its width in the present instance being 2.5μ. Naturally, there is a limit to the sharpness that can be measured under given conditions, so an actual knife edge should be measured to determine this limit. Furthermore, the slit must be accurately parallel to the edge of the image. For the traces shown, a series was made at successive orientations of the slit, and the trace with the steepest slope was subsequently selected to represent each image.

Ordinary microdensitometer traces, such as those shown, are on a transparency basis because photoelectric cells respond linearly to incident flux, and thus the sharpness is evaluated at a point midway in transparency between maximum and minimum. From a visual standpoint, it might be preferable to evaluate sharpness at a point midway in *density* between maximum and minimum, which would involve logarithmic amplification. The traces made on a transparency basis are not readily convertible because the transparency scale is so compressed at high densities.

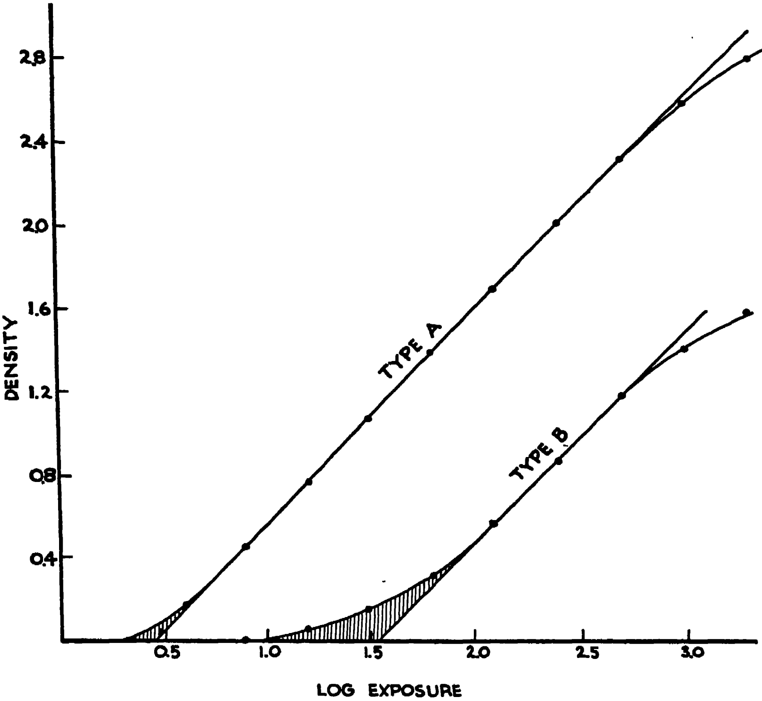


FIG. 324. Characteristic curves showing difference in toe shapes.

RESOLVING POWER

As the exposure to a multiple slit or grating is increased from a very low value, the slit images at first appear and become distinguishable, provided the grating is sufficiently coarse; but eventually turbidity results in an encroachment of the lines upon their neighbors, so the separate images again become indistinguishable. This ability of the emulsion to record fine detail may be termed broadly *resolving power,* and it clearly passes through a maximum as the exposure increases, as shown in Figure 325. If the resolving power is to be high, the characteristics of the emulsion must be such that the images will become sufficiently dense to outline the narrow lines before the intervening spaces fill up; in other words, γ must be high and turbidity low. These are also the requirements for a high value of sharpness, but other factors are involved so that sharpness and resolving power are not strictly proportional.

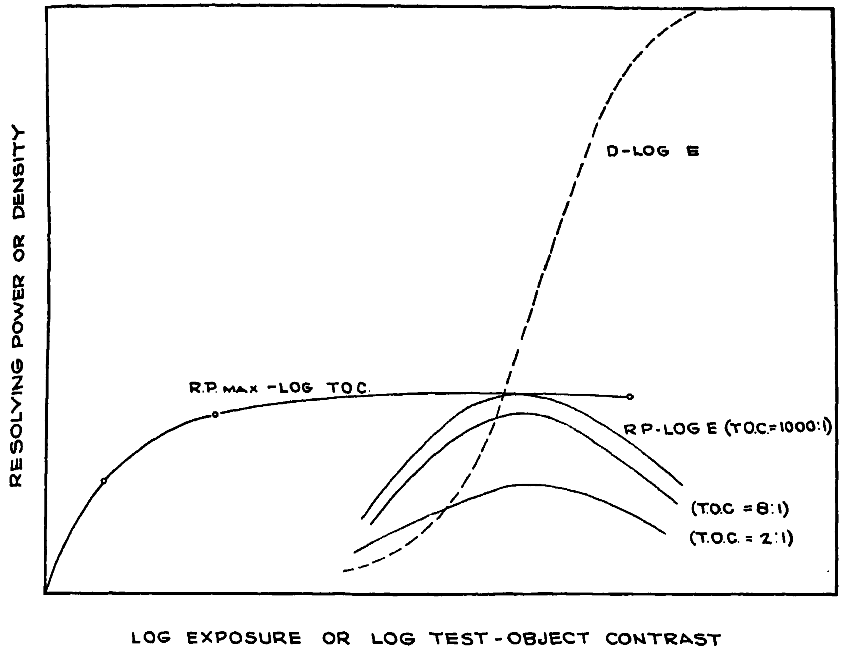


FIG. 325. Resolving power as a function of exposure for three values of test-object contrast and maximum resolving power as a function of test-object contrast. Eastman Process Plate. The broken line is the characteristic curve.

It is customary to state as the "resolving power" under any given set of conditions the maximum value obtained as the exposure is varied. The corresponding values of exposure and density, respectively, are sometimes called the *optimum ex-*

posure * and the *optimum density.* Although resolving power is less fundamental in an analytical sense than the characteristics previously discussed, the ease with which it can be measured and its practical significance as indicating the over-all performance of a material have resulted in the development of several techniques of measurement and the acquisition of a considerable amount of information concerning it.

The test object can be printed on the sample either by contact or by projection. In the former case, the test object must have a higher resolution than that of the best material to be measured. This is difficult to attain, and photographing a master chart on a Lippmann emulsion with a camera of adequate resolving power is perhaps the best solution. Furthermore, it is essential that the contact between test object and sample be perfect. The mortality of test objects, because of mechanical injury, is heavy; on the other hand, no question of the resolving power of a lens can be raised nor is there any focusing problem.

The more common procedure is to use a camera, in which case the test object is less difficult to make because it can be comparatively large. The choice of lens is important. Narath[51] has shown that a microscope objective is suitable but that a photographic objective is not. At the Kodak Research Laboratories, an $f/5.3$ telescope objective of 153 mm. focal length is used, the reduction being 75 times. Since the field angle is less than one degree, the performance is excellent. According to optical theory, the resolving power should be

$$N = \frac{1000}{1.2(f/\text{-number})\lambda}, \tag{34}$$

where N is in lines per millimeter and λ is in microns. The result is 300 for this lens, and experiment confirms this figure. Microscope objectives are more suitable for use with materials of extremely high resolving power. In Narath's apparatus, a series of exposures at different focus settings is made on a single sample; in the Kodak apparatus, a power-of-two time-scale exposure series at a predetermined focus setting is made, since the focus has been found to remain steady, but a focus test is also run at the optimum exposure when testing materials of high resolution.

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* This term is the same as that used to mean the most efficient exposure in Chapter VI, but there is no connection between the two meanings.

The pattern of the test object is of importance. In optical theory, a double star is usually adopted for the sake of theoretical simplicity, but a linear pattern is more suitable for photographic work. The fan type shown at *A* in Figure 326 is fairly easy to prepare and will cover a wide range if several copies are made to different scales, but it is a difficult type to evaluate. The same criticism applies to the type of pattern shown at *B*. Probably the most generally satisfactory type is the one designed by Sandvik and shown in Figure 327. The line interval represented by each set of three varies from that of its neighbors by 5 or 10 lines per millimeter. Using a similar pattern, Ross[52]

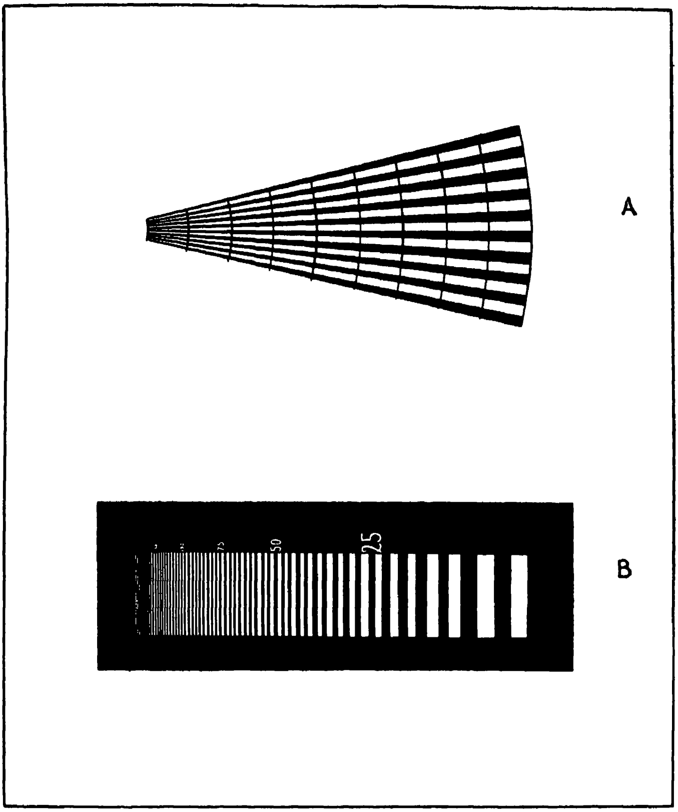

FIG. 326. Types of resolving-power test object.

showed that the fan type gives results that are systematically low, while a double-star pattern gives approximately the same results. The reverse or negative of Figure 327 gives much lower results because of the flare arising from the background.

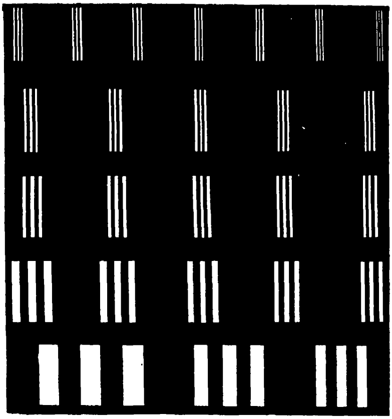

FIG. 327. Standard parallel-line test object.

The sample after development can be examined in an ordinary microscope, preferably one having a binocular eyepiece. A magnification of approximately 100×, using a 10 × (16-mm.) objective, is suitable. A ribbon-filament lamp arranged for Köhler illumination is an excellent source. In this arrangement, the filament is imaged on the substage iris with the lamp condenser, and the latter is imaged on the sample with the substage condenser. Thus, the aperture and the field can be varied in size independently of each other. A bright light source that can be reduced at will with a rheostat is required because some emulsions have high optimum densities. For such emulsions, a diaphragm of the proper size and shape at the lamp condenser to cover everything but the dense image is essential to avoid glare.

An unusual type of apparatus has been designed by Bruscaglioni.[53] It consists essentially of Young's interferometer behind a monochromator, but the interferometer has been modified by the addition of a cylindrical lens and the two members of the double slit are curved. The image on the sample is an interference pattern like a double fan having a common apex but with the ribs extending in opposite directions. The reading is made by means of a scale in the observing microscope that is calibrated in terms of the length of the portion of the pattern centering on the common apex that is below the limit of resolution. Such an apparatus can be used for monochromatic light alone; a similar apparatus has been devised by Crino [54] for white light. In this apparatus, the fringes are formed by the interference of overlapping spectra produced by a diffraction grating whose central portion is stopped off.

Although the relationship of other characteristics of the emulsion to resolving power is obscure, the effects of certain conditions are well established and the effects of others have been studied for a limited number of emulsions:

1. Line/space ratio in test object: It was early supposed that the ratio of the width of the lines to that of the intervening spaces was without effect on resolving power; but Sandvik,[55] by using the test object reproduced in Figure 328, showed that a linear relation exists between resolving power and the logarithm of this ratio, which he designated A. It is customary now to make $A = 1$ unless otherwise specified, and the error to be expected from a variation in the ratio is approximately

$$\delta R = -35\,\delta \log A$$

according to Sandvik's data, the exact amount depending upon the emulsion. The method of maintaining the line/space ratio during the preparation of a test object has been discussed in the preceding section.

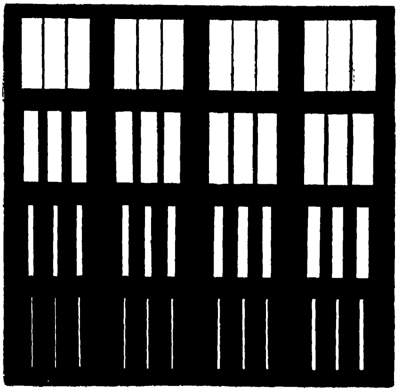

FIG. 328. Parallel-line test object of varying line/space ratio.

2. Test-object contrast: The resolving-power curves of Figure 329 are for three values of the brightness of the background of the test object with respect to that of the lines. When the maximum value of resolving power is plotted against the logarithm of the test-object contrast, an exponential curve results, as shown. Sandvik[56] studied this relation for four emulsions, plotting resolving power against the density of the background of the test object, since the lines were all practically clear. If the maximum resolving power in each case is set at 100, Figure 329 shows that the data in all cases are a good fit for a curve whose equation* is

$$R = R_{\infty}(1 - e^{-aD}) \tag{35}$$

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* H. Frieser[57] has given a theoretical basis to this equation as well as to the relation concerning the line/space ratio.

when R_∞ is taken as 100 and α as 2.20. Thus, the increase in resolving power is rapid when the test-object contrast is low but very slight for contrast values greater than 50 or so.

3. Level of illumination: The level of illumination in the image is not especially important within reasonable limits, as experiments at the Reale Instituto Nazionale di Ottica[58] have shown. Under conditions that produce decreased turbidity at lower levels, however, one would expect the resolving power to be improved, and Ross cites experiments in which resolving power increased about 15 per cent when the illumination level was reduced in the ratio 650 : 1.

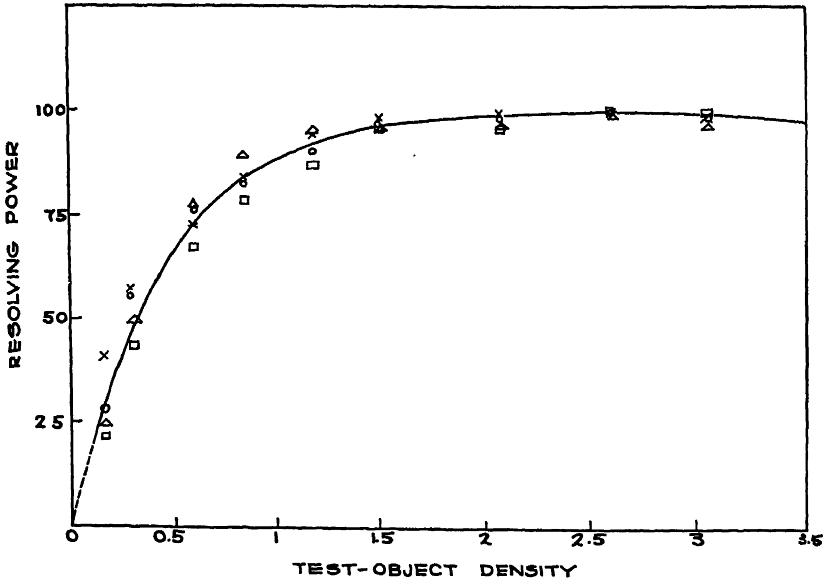

FIG. 329. Maximum resolving power for optimum exposure plotted as a function of the density of the test object (Sandvik). Four emulsions are shown; the values for each have been adjusted to give the same maximum.

4. The wave length of the light: Sandvik and Silberstein[50] made experiments that indicated a pronounced rise in resolving power in the blue end of the spectrum and usually a slight rise in the red. Later experiments, however, such as those made at the Instituto Nazionale, do not confirm the magnitude of the rise in the blue, although some rise is almost invariably exhibited. Probably this effect, like the variation of sharpness

in the same spectral region, is associated with the variation in the opacity of the emulsion. Sandvik's experiments indicated that the resolving power to white light is approximately equal to the *lowest* value found for monochromatic light; on the other hand, Crino states that it equals the *highest* value. The matter obviously requires further investigation.

5. Composition of developer: Early experiments seemed to indicate that the type of developer has a marked effect on resolving power; but Ross found the opposite, and later work seems to confirm his results. Some fine-grain developers will improve the resolving power of some emulsions, but this is not a universal characteristic of such developers.

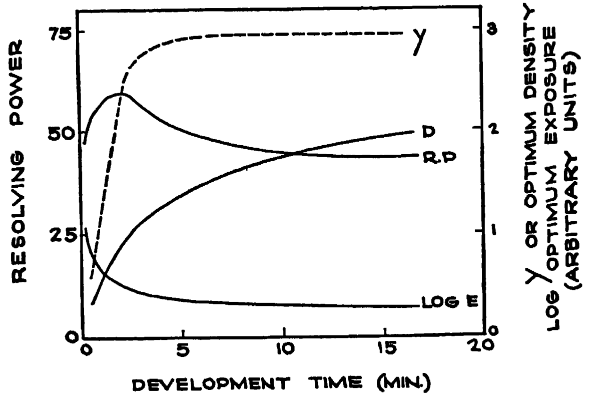

Fig. 330. Maximum resolving power of Eastman Process Plate, optimum density, optimum exposure, and γ as functions of the development time.

6. Development time: As development progresses, the resolving power rises rapidly to a maximum, drops somewhat, and then remains approximately constant, as Figure 330 shows. The optimum exposure is but little affected for long development times, but the optimum density rises slowly. Several types of emulsion have been examined at the Instituto Nazionale, and all behaved in somewhat this manner.

7. Developer concentration: The Instituto Nazionale results indicate that, in the case of a typical metol-hydroquinone developer, holding the development time constant while increasing the concentration produces an effect on resolving power similar to that produced by holding the concentration constant while increasing the time, as just described.

8. Developer temperature: There is frequently some reduction in resolving power as the temperature of the developer is raised, the Instituto Nazionale investigators claim. At the same time, the optimum exposure is reduced and the optimum density raised.

9. Reduction and intensification: Long ago, Scheffer[59] had shown that the resolved image resides only at the surface of the emulsion and that fine structures on emulsions of high resolving power can be entirely destroyed by a brief treatment in Farmer's reducer without greatly affecting the total density. More recently, the Instituto Nazionale investigators found that ferricyanide and permanganate, which are cutting reducers (Chapter XIV, p. 544), lower the resolving power and optimum density, whereas persulfate has little effect. In the dense regions of the negative, however, they found that reduction of any kind improves resolution. On the other hand, intensification has no certain effect on the maximum resolving power although it raises the optimum density slightly.

10. Dyes: It is well known that dyeing an emulsion yellow increases its resolving power for blue light; it may double it, though with a serious loss in sensitivity. The most obvious explanation is that the turbidity is decreased by the absorption of light and that the image is confined to the surface of the emulsion.

11. Silver halide concentration: The maximum resolving power is almost independent of silver halide concentration, according to Trivelli and Smith;[60] but, at a given image density, provided it is high, the resolving power can be more than doubled by tripling the concentration.

12. Grain characteristics: With the silver halide concentration held constant, Trivelli and Smith found that a small grain size (and a correspondingly large number of grains) results in a much better resolution than a large grain size. There are two reasons for this: In the first place, the grains in their emulsions were more nearly alike in size when they were small or, to express it mathematically, the standard deviation of the size-frequency curve was small; and it has long been known that a narrow range of grain sizes is favorable to good resolution. This accords with the influence of desensitizers, as described

by Ross. They improve resolution and narrow the range of grain size by acting differentially with respect to size. In the second place, a coarse-grain material is physically incapable of high resolution. For this reason, fine grain and good resolution are frequently considered synonymous. It may be an exaggeration to say, with some authors, that granularity and resolving power to a linear test object are independent, but experience does indicate that the order of a series of emulsions on a resolving-power basis is rarely the same as on a granularity basis although the effects may be parallel.

13. Shape of resolving-power curves: Crino[61] claims that the shape of the curve of resolving power against log exposure is constant as the independent parameter (*e.g.*, developer temperature, concentration, etc.) is varied and that it can be described by the general formula

$$R = c \frac{(\log E)^a}{b^{(\log E)}}, \qquad (36)$$

where a, b, and c are constants for a given group of curves. As the parameter is varied, the intercept of the curve migrates along the log-exposure axis, of course, and a general expression for a family of curves can be derived by introducing the equation for the migration of this intercept into the simple equation above. More extensive tests are required to establish the universality of this equation.

Many of the statements made above are generalizations based upon a very limited number of experiments which themselves are often contradictory in details. A vast amount of work must be done before the effects of the various conditions can be determined with certainty, and still more before the effects can be correlated.

With so many influences affecting resolution, it might be questioned whether one may usefully speak of *the* resolving power of a material. The conditions under which the determination is made must be understood, of course, and certain conventions have been tacitly accepted. At the Kodak Research Laboratories, by the unqualified term "resolving power" applied to a given material processed according to a given technique is meant the maximum number of lines per millimeter that can be distinguished visually in the developed image under adequate illumination and magnification, regardless of exposure, ordinary heterochromatic light (daylight or tungsten quality, and ultraviolet being filtered out if desirable from the standpoint of lens aberrations) being used for the exposure, the test object consisting of parallel, clear lines of practically infinite length on an opaque ground, the lines and intervening spaces being of equal width.

The order of magnitude of the resolving power of ordinary films is 50 lines per millimeter. Fast emulsions formerly showed values as low as 30, but improvements in emulsion manufacture have raised the value of some of even the fastest emulsions to 45. The fine-grain films for miniature-camera work are capable of reaching 70, while those designed for duplicating motion pictures and for microphotography extend to 130 or more. The ordinary and the fine-grain sound-recording films whose turbidity and sharpness characteristics were shown in the preceding section have resolving powers of 50 and 150, respectively. For years, albumin and collodion plates with values of 125 or so held the record for ordinary materials; but fine-grain, thin-coated films for photomechanical reproduction with values well over 200 are now on the market. A special material of the Lippmann type is available with a resolving power higher than 300. The resolving power of the Lippmann emulsions must be very high, but the highest measured value for any material is probably that obtained by Goldberg[62] and confirmed by Narath.[63] Goldberg used a collodion-chloride emulsion that he exposed through a 4-mm. apochromatic microscope objective to form a print-out image. He held the plate against the end of a tube during the exposure and focused by grinding the end of the tube with a piece of ground glass, using no abrasive. Narath used a 3-mm. apochromat but focused with an ordinary screw. Both attained a resolving power of 1000 lines per millimeter, which corresponds to a line width of the order of a wave length of visible light and, hence, only on the verge of resolution optically.

Although resolving power is customarily expressed in lines per millimeter, there is no reason why it should not be expressed as the width of the corresponding lines, and Narath [64] points out that this would represent the wave length of the corresponding tone on a sound record. The frequency of this tone would be

$$f = v/\lambda, \tag{37}$$

where v is the speed of the film, which is 45.6 mm. per sec., and λ is twice the width of the narrowest resolvable line. But this application of resolving power as it is usually measured is not especially significant. In the first place, the material would have a lower resolving power for a sinusoidal light distribution than for the square-topped distribution characteristic of the usual test object. In the second place, there is no reason to suppose that the visual limit of resolution is equivalent to the highest frequency that can be reproduced from a sound record.

The characteristics of a photographic material must always be considered in relation to the particular application of the material. It has been assumed here, for instance, that the optical image is sharp, in which case photographic sharpness and resolving power decrease with increasing diffusion of the light. But, in astronomical photography, the atmospheric unsteadiness is so great as to overshadow the diffusion in the emulsion, and thus the controlling factor is contrast. This dictates the selection of a material of high γ regardless of turbidity. Yellow-dyed plates, although having good resolution, have been found entirely unsuited to astronomical photography because their good resolution is a consequence of their low turbidity, which is accompanied by a comparatively low contrast.

With increasing use of the electron microscope, the resolving power of emulsions for electron beams is becoming important. Not much work has been done in this field, but von Ardenne [65] has made a brief investigation of the minimum width of track that certain emulsions will reproduce. As the accelerating potential is raised, the penetration of the beam into the emulsion increases; and von Ardenne shows that the resolving power is at a minimum when the penetration depth of the electrons is slightly greater than the emulsion thickness. Inasmuch as the width of track is determined largely by scattering within the emulsion and this scattering is produced mostly by the gelatin, he points out that the most favorable material is one that is poor in gelatin, such as a Schumann plate. Under comparatively unfavorable conditions, he was able to produce a track only 6 μ wide on such a plate.

DISTORTIONS AND MOVEMENTS OF THE IMAGE

Photographic materials cannot be used for mensurational purposes without a study of characteristics that might introduce spurious effects. That paper is quite out of the question as a base if any accurate position measurement is to be made goes without saying.. Ordinary film is much better; but for such purposes as aerial mapping, a special base of low shrinkage is required.* Even plates are not perfect when measurements must be made in terms of microns; here there enter (1) large-scale distortions, (2) the gelatin effect, (3) the turbidity effect, and (4) the Kostinsky effect.

1. Large-scale distortions. Ross discovered that certain drying conditions produce a general expansion of the gelatin layer, amounting to one part in twelve hundred on plates one inch square, but that this disappears upon soaking and drying in still air. Even ordinary air drying may introduce a probable error of 2μ. This can be reduced by half if the plate is dehydrated in alcohol before drying.† The error is especially marked near the edge of the plate. Drying starts at the edge, and the gelatin with its encompassed images migrates toward the dried region as the drying line moves inward. The effect is not present beyond approximately a centimeter from the edge.

In the investigations reported by Berndt, the test object consisted of a silvered-glass plate on which were scratched lines (*a*) on the diagonal, (*b*) through the center parallel to the edges, and (*c*) along the edges. The test object was printed on the plates by contact. Except for two or three plates (especially one double-coated plate) for which the errors were abnormally large, the error in measuring 100-mm. sections of the border lines was 15μ or less. Curiously enough, although the error of measurement along a diagonal might rise to 10μ, the error involved in measuring along the center lines parallel to the edges was of the order of only 5μ.

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* The mensurational characteristics of plates and films have been tested by Berndt.[66]

† A plate dehydrated by alcohol must be dried in a humid atmosphere (*e.g.*, a box lined with wet blotting paper) to prevent the emulsion from becoming cloudy.

Distortions amounting to upwards of 5μ were also found by Cooksey and Cooksey[67] even when special precautions were taken to dry the plates uniformly. These distortions they attributed to stresses introduced into the gelatin layer during manufacture and released during processing. By releasing the stresses before exposure, they reduced the distortions to a very low value. Their method was to pretreat the plates with water for thirty minutes and then with approximately 90 per cent ethyl alcohol for twenty minutes, after which the plates were dried. On the other hand, Van de Kamp and Vyssotsky[68] claim that distortions of the magnitude found by the Cookseys are uncommon and that this "normalizing" process is rarely required. The need for it should always be considered, however, especially when rare phenomena are to be recorded.

2. The gelatin effect (Ross effect). It was remarked in connection with turbidity that the reduction products formed during development seem to tan the image and retard the normal growth resulting from diffusion. Figure 314 showed this effect for various development times, in one particular case of an image approximately one millimeter in diameter. Ross investigated this phenomenon by means of a test object consisting of an opaque sheet in which holes had been cut, as shown in Figure 331.

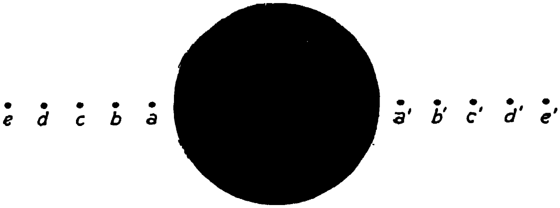

FIG. 331. Test object for image contraction and displacement.

The image of the central opening had a diameter of 1.75 mm. on the plates, and those of the small openings had a diameter of 50μ. The plates were measured before and after drying; the fixing bath contained no hardener. When pyro-metol developer was used and the central opening was covered, the separations *aa'*, *bb'*, etc., of the corresponding small images were sensibly the same whether the plate was wet or dry; but when the central opening was recorded, not only did its image shrink by 0.109 mm. on drying, but the distances *aa'*, etc., diminished by amounts that were greater for the inner images. In the case of a chlorhydroquinone developer, the shrinkage of the central disk was only 0.012 mm., and no certain effect was observable upon the separations of the small images.

To elucidate this behavior further, plates bearing star images were swollen with water, and photomicrographs were made of sections through the images. Figure 332 shows that hydroquinone (*A*) produces a slight excess swelling at the image; this developer produces little contraction of the dried image. On the other hand, pyrogallol (*B*) produces a very marked depression, and it was shown to produce a notable amount of contraction on drying. Further evidence of the violent physical effects produced by pyrogallol is given by *C*, which shows a fold in the gelatin between two close images. Such effects are not absent even when the plate is dry because disturbed optical conditions are sometimes noticed at the edges of images when they are measured. Furthermore, such effects appear to be associated with the contraction effect, which is produced mainly by pyro and caustic hydroquinone developers.

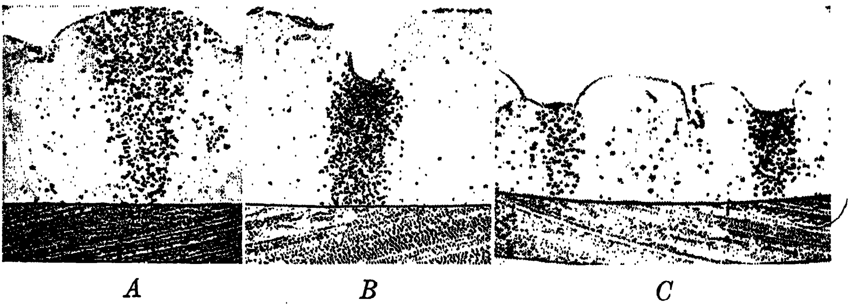

FIG. 332. Photomicrographs of cross sections of star images: *A*, hydroquinone developer; *B*, pyrogallol developer; *C*, rupture of emulsion between images developed in pyrogallol.

The mechanism of the phenomenon is clear on the assumption that the reduction products of the contracting developers tan the gelatin. This takes place within the image, which, therefore, contains less water than the surrounding gelatin and dries more rapidly. As it dries, it sets up internal stresses that the surrounding gelatin cannot withstand while wet, and the drier gelatin contracts. The stresses must be balanced within the interior of a large image; and Figure 333, indeed, demonstrates that the effect is practically constant for images greater than 5 mm. in diameter. The amount naturally depends upon the developer, but for this particular unspecified developer, the contraction is limited to a distance of 2.5 mm. from the edge. The surrounding gelatin is pulled toward the image, of course, as the experiment described in connection with Figure 332 proved. This contraction produced by the tanned gelatin has come to be called the *Ross effect.*

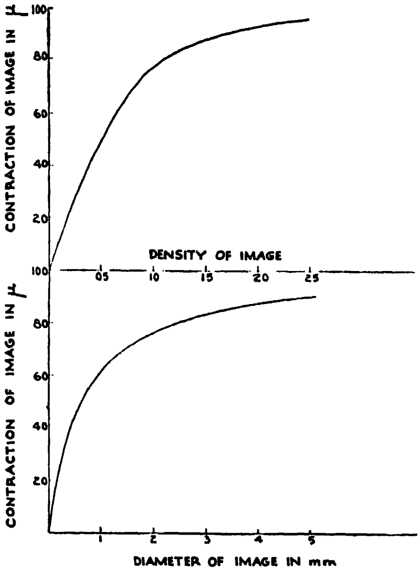

FIG. 333. Contraction of a star image as a function of its density and of its diameter (Ross).

The practical result of this effect is shown in Figure 334, which is a set of turbidity curves from Ross. The diameter law is strictly obeyed for the smallest images, although Figure 334 indicates that the rate of growth is about 12 per cent less than it would be if the Ross effect were absent. Since this effect is constant for the largest images, despite the variation in diameter, one would expect the turbidity to be low until the diffusion becomes great enough to neutralize the Ross effect. Actually, the turbidity is negative, and this may possibly be accounted for by the increase in the Ross effect as the image density increases in the low-density range.

A double-star image should obviously be considered as a unit, which means that the components will approach each other. Ross states that, "for the close doubles of separation 0.1 mm. or less, the contraction due to the movement of the gelatin is 1.6μ for all ordinary developers." A notable exception is pyro-metol, which produced almost four times as much contraction. It is clear that the same effect should appear in the case of neighboring spectral lines, and Ross found that its magnitude depends merely on the width of the lines and not at all upon their length.

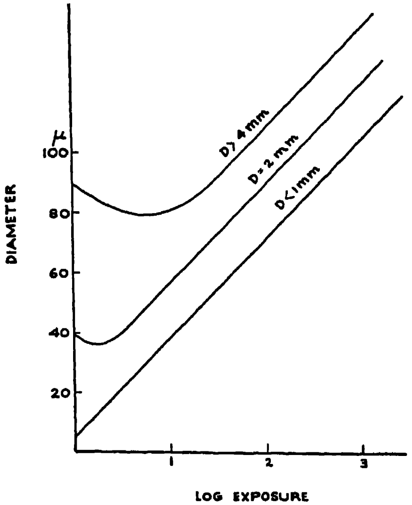

FIG. 334. Variation of the diameter of a star image with change in exposure for three sizes of geometrical image (Ross).

3. The turbidity effect. If two point images are close together, the diffused light from each will reinforce that from the other in the intervening space, so the family of equiluminous curves will be of the shape sketched in Figure 335. The developed image under any set of exposure and development conditions is bounded by one of these curves if spurious development effects are absent, which means that the developed images are elongated along the line of centers. Since this elongation is exclusively inward, the centers are displaced toward each other, and the separation between centers is diminished. On the basis of Bouguer's law, it is easy to show that the total displacement of the centers δ is related to the distance between the separation of the adjacent edges of the images r by the equation

$$e^{k\delta} = 1 + e^{-kr}. \tag{38}$$

The turbidity effect cannot be measured directly for reasons that will presently appear, but it can be found by making a graded series of exposures to a point object to obtain Δ. Since

$$\Delta \cdot k = 1.39 \quad \text{(See equation (29), p. 889)}$$

and r can be measured on the plate, the value of δ can be found. The magnitude of the effect can be seen from Figure 336, which covers the usual range of values of Δ from 10μ to 30μ.

4. The Kostinsky effect. If an attempt is made to measure the turbidity effect experimentally and the plate is measured before drying to avoid the gelatin contraction, the images will

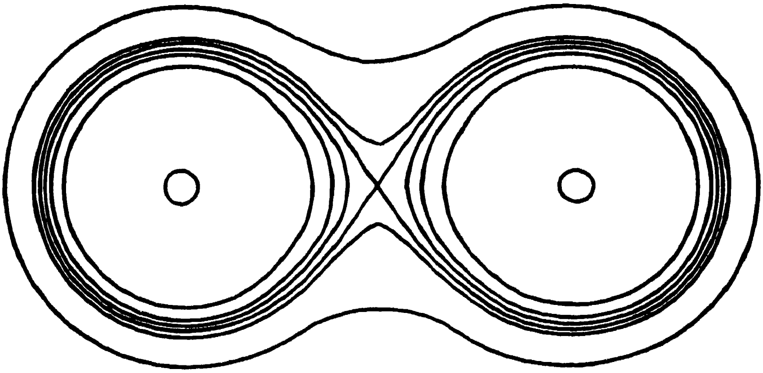

FIG. 335. Equiluminous curves around neighboring images of equal circular sources.

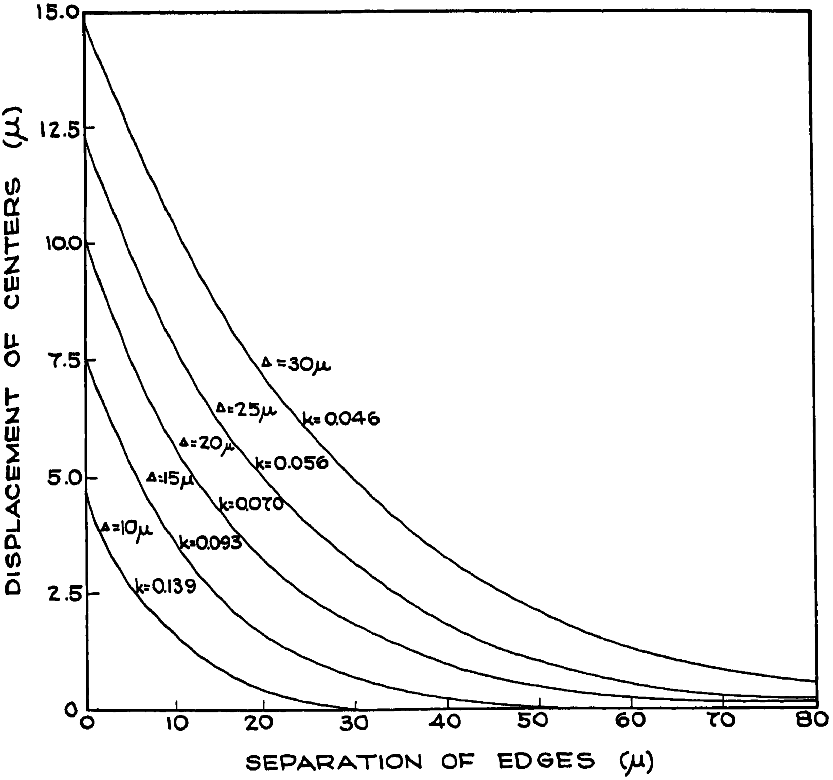

FIG. 336. Theoretical displacement of centers of neighboring star images as a function of the separation of their edges.

separate instead of approach each other as they become larger with increasing exposure. Even after drying, the gelatin contraction is not sufficient to overbalance this repulsion if the edges of the images are closer than about 40μ. Kostinsky gave the reason in 1906, when he pointed out that the developer is more nearly exhausted in the space between the images than at the outer sides and that the bromide concentration resulting from development is greater at the same time. This is the explanation later advanced by Eberhard to account for the diminution of density at the edge of an image; but, in the present instance, the result of interest is that the inner boundaries of the images are less developed than the outer. Moreover, the effect is the more pronounced, the closer the images approach each other, just as is the turbidity effect; but the Kostinsky effect is active at greater distances than is the latter.

If, instead of making the images approach each other by means of overexposure, the geometrical images are brought closer together, there is less development action for the same image separation, and the Kostinsky effect should be reduced. Such, indeed, is found to be the case. The sign and magnitude of the displacement of the centers in any given case, then, must be determined by a study of the particular conditions involved.

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CHAPTER XXII

PHOTOGRAPHIC ASPECTS OF SOUND RECORDING

The physical phenomenon termed *sound* consists of rapid variations in atmospheric pressure ordinarily produced by the vibration of mechanical parts or of columns of air, as in wind instruments. If the rate of vibration lies between about 16 and 20,000 cycles per second, the result is a note of audible frequency.* From a mathematical standpoint, the simplest type of variation in sound pressure is a pure sine wave, represented by

$$p = P_0 + P \sin \omega t, \tag{1}$$

where P_0 represents the average atmospheric pressure, upon which is superimposed a sinusoidal variation of amplitude P. Although a simple sine wave of this sort is rarely produced by a musical instrument, any musical note may be analyzed as a fundamental sine variation plus a number of harmonics or overtones.† Each of these, however, is itself a simple sine wave whose rate of variation is an integral multiple of the fundamental. The quality, or timbre, of a musical instrument depends upon the relative amplitudes of these harmonics.

If the sound waves impinge upon a microphone, they produce small electric currents, which can be amplified by electronic valves. If a perfect microphone and amplifier are used, the current, i, in the last stage of the amplifier may be represented as

$$i = I_0 + I \sin \omega t. \tag{2}$$

The amplified electric current may be used to control the beam of light which falls upon a motion-picture film moving through a camera, so that the sound waves are represented as variations in the form or density of the *sound track.*

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* The exact limit of audibility depends upon the intensity of the source and the characteristic of the observer's ear.

† The fundamental frequency of the A below middle C is a little more than 200 cycles per second. Assuming it is exactly 200 cycles per second, this note will consist of the fundamental 200-cycle variation plus a second harmonic with a frequency of 400 cycles per second plus a third harmonic with a frequency of 600 cycles per second, and so on.

The sound track is printed upon the positive film and occupies a position between the picture area and the perforations of the film, as seen in Figure 337. When the sound track passes through a very narrow beam of light during the projection of the picture, the intensity of the light transmitted by it varies rapidly and continuously in the same way as the air pressure representing the sound by which the record was produced. By means of a photoelectric cell, the transmitted light is converted into electrical energy which, after amplification, actuates a loudspeaker and reproduces the sound. The cycle of operations concerned in the recording and reproduction of sound may, therefore, be visualized somewhat as shown in Figure 338. A source of sound, I, emits pressure waves which the microphone, II, converts into electrical energy. This is amplified and operates a galvanometer of special type, IV, so designed that the variations in electrical intensity are transformed into variations in a beam of light. These variations are recorded on a moving film at V. The film is developed, VI, and printed on a positive film, VII, which is developed and, in the projector, controls the intensity of a beam of light from a lamp, IX. The light transmitted by the film falls upon a photoelectric cell and is converted into electrical energy. This, after amplification, operates the loudspeaker, XI, which reconverts the electrical energy into sound. The reproduction thus takes place through six transformations: The sound is converted into electricity, the modulations of which are transformed into variations of the light beam; these are followed by the chemical transformations of the photographic process, which take place in the four stages, V, VI, VII, and VIII; in stage IX, the silver deposit produces changes of light

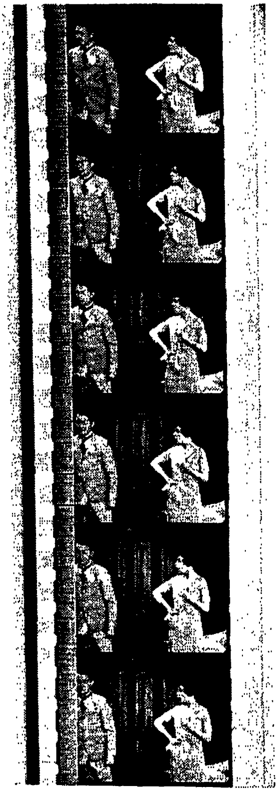

FIG. 337. Film with variable-density sound record.

intensity, which are transformed into electrical variations and these, in turn, into sound by the loud-speaker.

For ideal reproduction, the sound reaching the audience, XII, should be of exactly the same character as that reaching the microphone, II, the intensity, of course, being adjusted by appropriate control of the amplifier. The original sound consists of a complex mixture of simple sounds varying particularly in the frequency and relative intensity of the different components; and, for satisfactory quality of reproduction, the relative intensities of the different frequencies and the actual form of the pressure waves must be preserved within certain limits throughout the series of transformations. This involves many problems in the

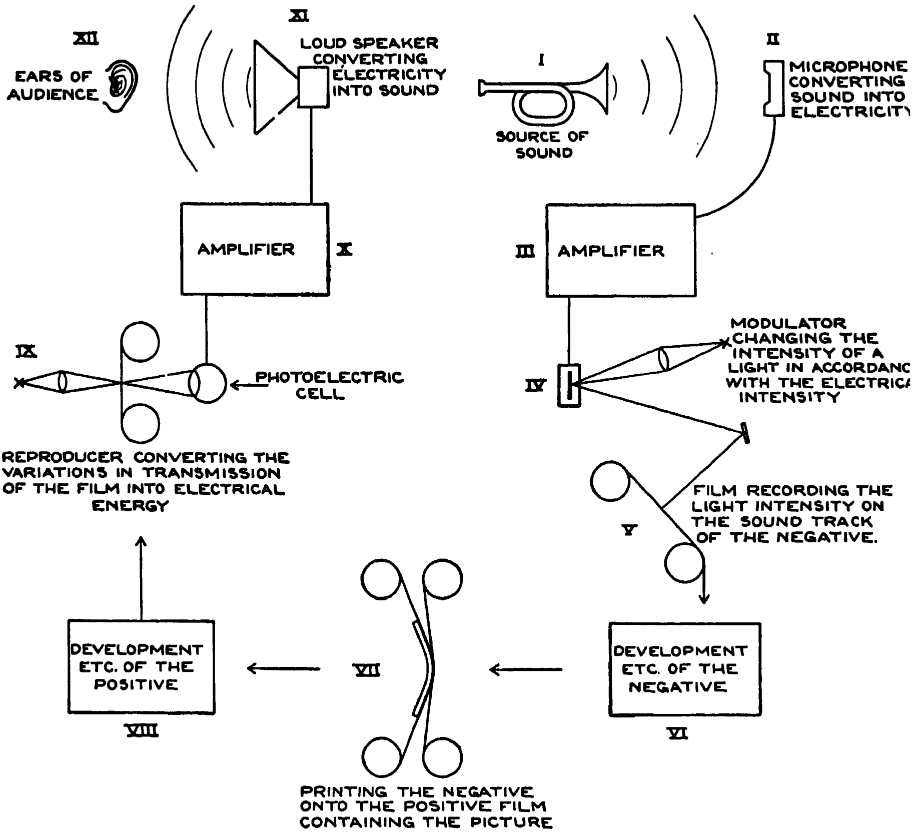
XII
EARS OF AUDIENCE
XI
LOUD SPEAKER CONVERTING ELECTRICITY INTO SOUND
I
SOURCE OF SOUND
II
MICROPHONE CONVERTING SOUND INTO ELECTRICIT
AMPLIFIER
X
III
AMPLIFIER
IX
PHOTOELECTRIC CELL
IV
MODULATOR CHANGING THE INTENSITY OF A LIGHT IN ACCORDANC WITH THE ELECTRIC INTENSITY
REPRODUCER CONVERTING THE VARIATIONS IN TRANSMISSION OF THE FILM INTO ELECTRICAL ENERGY
FILM RECORDING THE LIGHT INTENSITY ON THE SOUND TRACK OF THE NEGATIVE.
V
DEVELOPMENT ETC. OF THE POSITIVE
VII
DEVELOPMENT ETC. OF THE NEGATIVE
VIII
VI
PRINTING THE NEGATIVE ONTO THE POSITIVE FILM CONTAINING THE PICTURE

FIG. 338. Cycle of operation in sound recording.

design of the acoustical and electrical apparatus and circuits, a discussion of which does not properly lie within the scope of this book. The discussion is restricted as far as possible to the operation of stages V, VI, VII, and VIII; that is, the properties of negative and positive photographic films and the conditions under which they must be used to insure satisfactory reproduction of sound.

In the reproduction of sound according to the cycle shown in Figure 338, the photographic operations involve the following factors for the control of the process:

A. The choice of the film for making the sound record
B. The amount of exposure given the film
C. The development of the sound record
D. The choice of the positive film
E. The exposure used for printing the sound record upon the positive film
F. The development of the positive film.

Since factors *D* and *F* are involved in the processes used for the production of the picture and must, therefore, fulfill the conditions necessary for the correct reproduction of its tones, they are more or less fixed and not available for the control of the sound record. For this purpose, therefore, factors *A*, *B*, *C*, and *E* are available. The positive film is that known as motion-picture positive, which by normal development has a γ of about 2.10 for the older type and about 2.50 for the newer, fine-grain type. This characteristic is set by the practice of the motion-picture industry for the production of pictures.

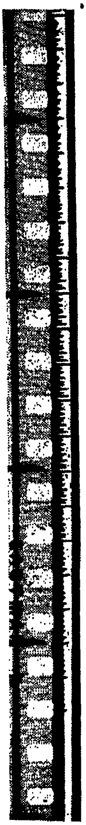

FIG. 339. Film with variable-area sound record.

Two distinct types of sound recording are in use, known as *variable density* and *variable area.**

The variable-density type of record is illustrated in Figure 337. The density across the sound track is uniform but is made to vary along its length by variations in the pressure produced by the sound at the microphone. A glow lamp or a string galvanometer operating as a light modulator is a familiar example of suitable apparatus for this purpose.

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* This latter term has become the generally accepted term for that type of sound record, although *variable width* is more descriptive.

For the variable-area type of record, the exposing light is of constant intensity and the sound record, therefore, of constant density; but the width of the track illuminated varies in accordance with the current of the microphone. An oscillograph whose mirror is adjusted to illuminate half of the sound track when there are no sounds at the microphone will produce the type of variable-width record shown in Figure 339. Other types of variable-width records are shown in Figures 344 and 346 and are discussed later.

The modulation, m, of the amplified microphone current, i, is defined as

$$m = \frac{i_{\text{maximum}} - i_{\text{average}}}{i_{\text{average}}} = \frac{i_{\text{average}} - i_{\text{minimum}}}{i_{\text{average}}}. \quad (3)$$

Since the maximum value of $\sin \omega t$ is 1 and its minimum value, -1, the maximum value of i is $I_0 + I$; the minimum value is $I_0 - I$; and the average value is I_0; it follows from equation (3) that

$$m = I/I_0. \quad (4)$$

If the variations in the exposure of the film are proportional to those in the current, I, the exposure of the film may be represented by

$$e = E_0 + E \sin \omega t, \quad (5)$$

where e is the value of exposure corresponding to a sound pressure p, E_0 is the value of exposure without sound before the microphone, and E is the maximum value of the sinusoidal variation of exposure.

The condition for correct photographic tone reproduction is simply that the illumination on the photoelectric cell of the reproducer be expressible by an equation in the form

$$i' = I_0' + I' \sin \omega t. \quad (6)$$

The constant term I_0' in equation (6) is independent of the constant term I_0 in equation (2). The amplitude of the variable term in equation (6), however, must be proportional to the variable term in equation (2); that is, the transmission of the positive sound track must be linearly related to the exposure of the negative. The transmission of the positive sound track will vary, therefore, from an average value T_0 to a maximum value $T_0 + T$ and a minimum value $T_0 - T$; and T/T_0 is the modulation. In the case of a variable-area record, the modulation is proportional to the width of the track covered by the silver deposit—the average transmission corresponding to half the width being covered; the maximum transmission, to the whole track being clear; and the minimum transmission, to it being completely covered.

In either type of sound record, the average transmission exists when no sound strikes the microphone. The transmission of the film, however, is not absolutely constant, owing to surface imperfections, such as dirt, dust, and scratches, and to the granular structure of the silver deposit. These changes in transmission cause a certain minimum of modulation, which, converted to sound, is known as *background noise.**[1]

Sound has three attributes: †

1. intensity or loudness
2. frequency or pitch
3. wave form, quality, or timbre.

For faithful reproduction of sound, all three attributes should be perfectly reproduced.

The maximum level of loudness is limited by the amplification factor, or *gain,* and the power-handling capacity of the electrical sound-reproducing system. The range of loudness levels, however, is determined by the minimum and maximum modulations that can be used. The minimum useful modulation, or transmission change, is limited by spurious changes in transmission; while the maximum permissible modulation is limited by the tolerable amount of wave-form distortion. Photographic material places no limit on the lowest frequency that can be reproduced; but its sharpness, resolving power, and astrogamma limit to a certain extent the highest frequency range that can be reproduced satisfactorily. As to wave form, the reproduction is dependent upon the fulfillment of certain specific requirements in the photographic operations.

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* Background noise is often referred to as *ground noise.*

† Sound has other characteristics, such as perspective; that is, the spatial distribution of the source and the binaural perception of the listener, which do not fall within the scope of the present discussion.

1. The Reproduction of Loudness

In systems where sound is reproduced by means of electrical circuits, the relative loudness or intensity is usually expressed in terms of the electrical transmission unit, the *decibel.*[2] If the electrical energy in a circuit is diminished to one-tenth of its input level, the loss, or attenuation, is stated to be ten decibels, the number of decibels being ten times the logarithm of the ratio: power output/power input. Correspondingly, if one sound has twice the energy of another, its power level is said to be three decibels (10×0.3, *i.e.*, $10 \times \log 2$) greater; if it has ten times the energy, its power level is ten decibels higher; one hundred times the energy, twenty decibels; and so on. A change of one decibel is practically the smallest change in loudness which the ear can recognize, *i.e.*, about 12 per cent. The intensity of sound is usually stated as the number of decibels above the *audibility threshold* of 4×10^{-16} watts per square centimeter. A soft whisper at a distance of three feet would be 15–20 decibels above this threshold; speech, 60–80 decibels; the range of an orchestra, from 40 for a single instrument pianissimo to 115 for the whole orchestra fortissimo.

As already stated, the maximum intensity of the sound produced from a given track can be increased to any reasonable extent by increasing the amplification between the photoelectric cell and the loud-speaker; but this amplification increases proportionately the minimum intensity of background noise, and the ratio between the maximum and minimum intensity remains constant. This ratio can be increased, however, by the methods known as *noiseless recording.* Other sources of noise are photoelectric-cell hiss,[3] *"shot-effect" hiss* in the amplifier circuit due primarily to thermal agitation,[4] and various microphonic noises caused by mechanical vibrations in the projector. These may be called *system noises.* In a well-maintained sound projector, the level of system noises is lower than that associated with the film.

The background noise due to the granular structure of the photographic image varies with the grain size of the emulsion

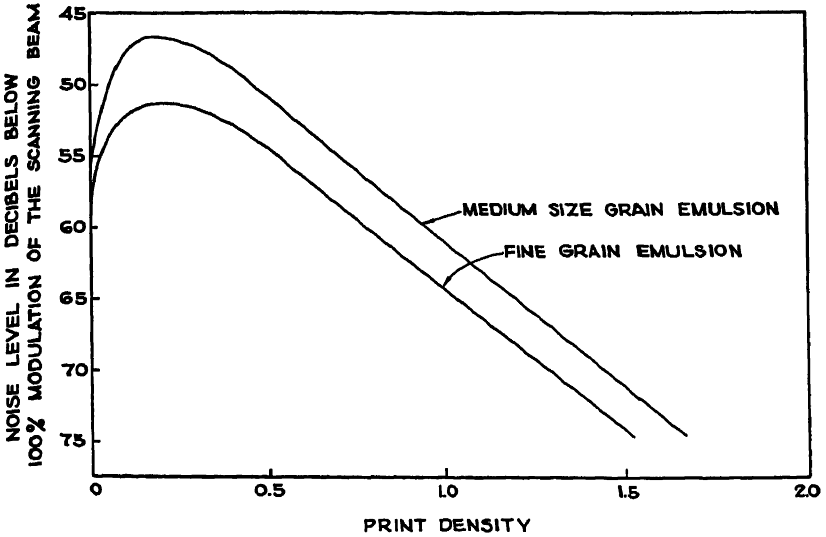

Fig. 340. Ground noise as a function of the density of a variable-density sound track.

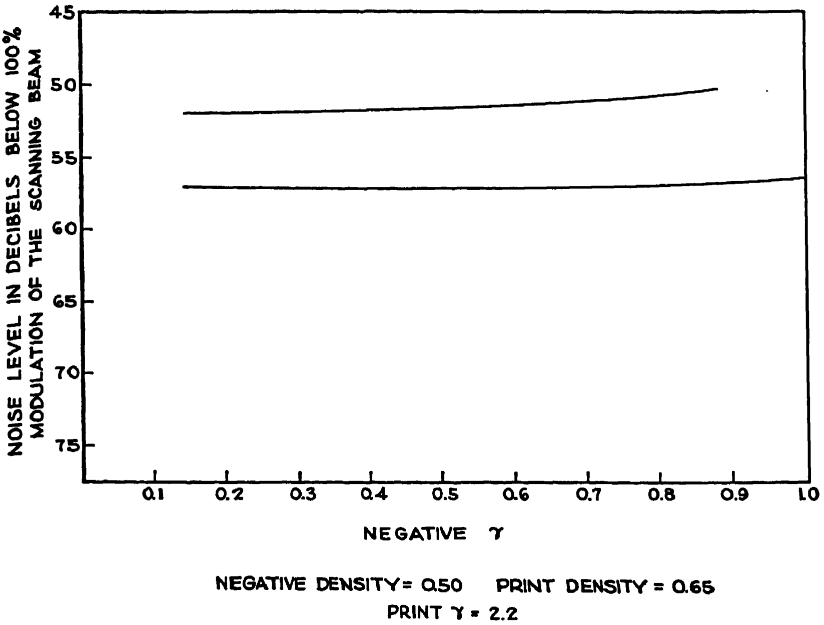

Fig. 341. Ground noise of variable-density prints on medium-grain and fine-grain films as a function of the negative γ.

and the density and γ of the developed image, as shown in Figures 340 and 341, respectively.[5] Figure 340 shows that above a diffuse density of about 0.2 the noise level diminishes as the density increases. It is evident that the background noise due to dirt and scratches on the film surface decreases as the density increases, because a given scratch or opaque particle in the scanned area of a sound track whose transmission is high produces a greater change in the photocell illumination than one in the scanned area of a track whose transmission is low. Since the background noise is most noticeable during silent passages, becoming less and less noticeable as the level of the recorded sound increases, the background noise could be effectively diminished if the average transmission of the positive sound track decreased with the sound level. In variable-density recording, this can be accomplished if the density of the positive sound track varies inversely with the modulation.[6]

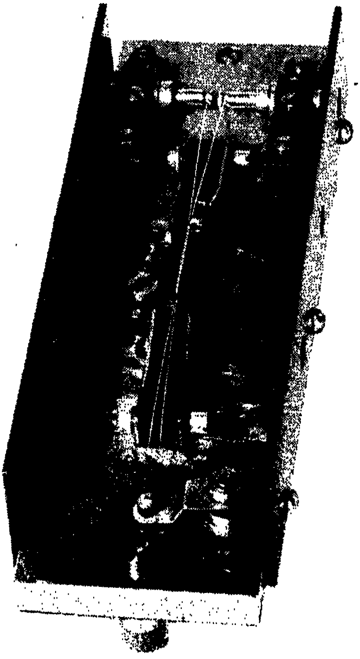

FIG. 342. The light valve.

In variable-density recording, the exposure of the negative film is made through a light-modulating device called a *light valve*,[7] shown in Figure 342. It consists essentially of two flat metallic ribbons placed under tension over two supporting members to form a narrow slit. In operation, these ribbons are placed in a magnetic field in such a manner that their spacing varies with the direction and magnitude of the amplified voice current from the microphone. This opening and closing of the ribbons determine the variation of exposure in the sound track.

In noiseless recording, the mean spacing of the ribbons is not constant but is reduced to some predetermined value during silent passages or periods of weak signals. This reduces the density of the negative unmodulated track and, consequently, increases the density of the positive unmodulated track, thus decreasing the background noise. As louder and louder sounds arrive at the microphone, increasing the valve modulation, the mean spacing of the ribbons increases sufficiently to accommodate the increased amplitude of the ribbon vibrations without bringing them together. In the normal method of recording, the ribbons have a constant average spacing, and their movements correspond to the variations of the sound current only. In noiseless recording, the ribbons may be said to have two motions: the motion due to the sound currents only, as in the normal method of recording; and a superimposed, slower movement related to the envelope of these sound currents. This is shown in Figure 343. Control of the ribbons is effected by a special electrical circuit that supplies to the ribbons not only the sound currents but another current at slower period corresponding to the envelope of the sound currents, as also shown in Figure 343. Thus, the exposure through the light valve on the negative film is reduced during periods of silence, while, at the same time, provision is made for increasing the

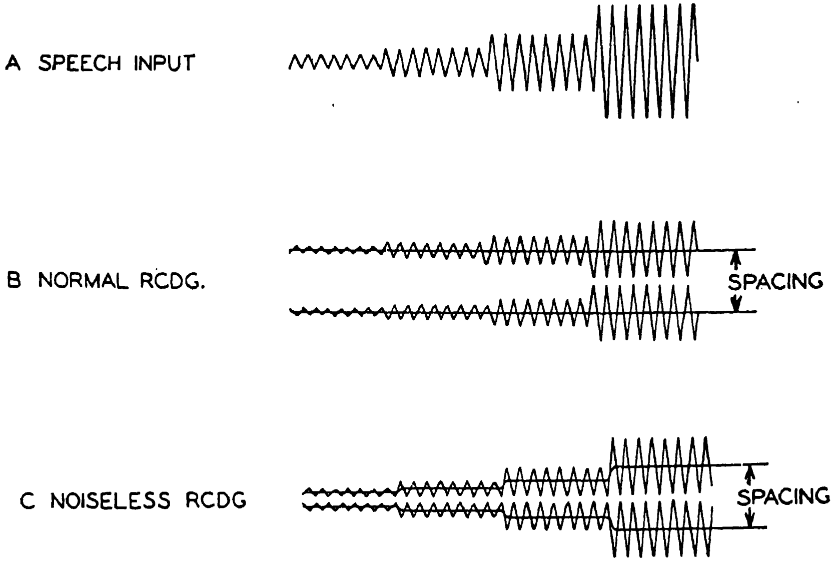

FIG. 343. Principle of noiseless recording.

average exposure automatically as the modulation of the light beam increases. It follows that the average density of the resulting negative sound track is at a minimum during silent intervals and increases to a fixed maximum with the level of the signal.

Turning to the variable-area system of recording, the same [8] result is achieved if the average width of the clear or unexposed portion of the positive sound track is less when the modulation is low and becomes greater as the modulation increases. In this system, any one of several types [9] of sound track (Figure 346) can be produced, depending upon the optical system. A galvanometer is so arranged that if a current such as the amplified microphone current flows through it, its mirror vibrates. Associated with this galvanometer are a source of illumination and an optical system which images one or more illuminated areas in the plane of the slit. The motion of these illuminated areas with respect to the slit is such as to vary the width of the sound track exposed in accordance with the change in sound pressure at the microphone. In passing, it is of interest to note the two general methods of modulating the length of slit illumination, as typified by the illuminated areas shown in Figure 345, whose motions, as a result of a variable current through the recording galvanometer, are parallel and perpendicular, respectively, to the major slit axis.

In Figure 344, the type of sound track used is produced by an illuminated area in the form of an equilateral triangle in the plane of the slit. Its base line is parallel to the major axis of the slit, and a perpendicular line drawn from the apex of the triangle to its base passes through the mid-point of the slit. The height of the illuminated triangle is large compared to that of the slit

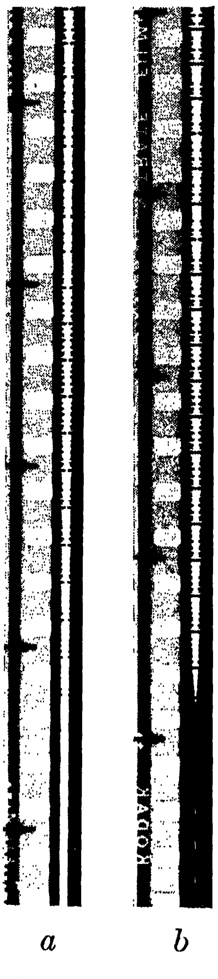

FIG. 344. Normal (a) and noiseless (b) variable-area sound records.

opening, so that only a small fraction of the light falling within the boundary of the illuminated triangle passes through the slit opening. For normal recording, the mean position of the triangle is adjusted so that the center of the slit opening lies at a distance from the apex equal to one-half of its maximum distance. Thus, when no sound strikes the microphone, the negative receives a uniform exposure. The strip of the negative exposed is centrally located in the sound track, and its width is equal to half that of the fully modulated track. When sounds strike the microphone, the triangular area vibrates on the slit, thus illuminating more or less of the slit opening, causing a corresponding increase and decrease in the length of the slit image on the film, with a corresponding widening and narrowing of the exposed area of the sound negative, which when developed and printed appears as shown in Figure 344a. The average position of the triangle is fixed, and the exposure through the slit results in a clear portion in the *positive* sound track sufficiently wide to accommodate full modulation; it is, therefore, much wider than that required for low modulation.

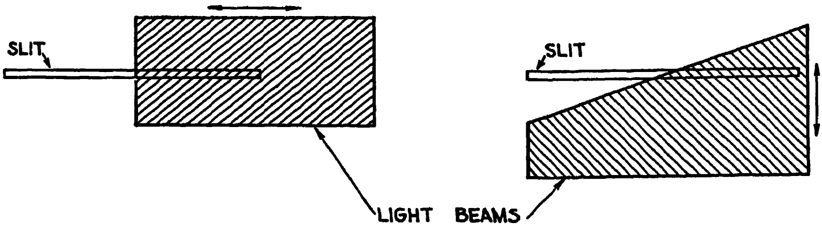

FIG. 345. Two methods of modulating the length of slit illumination in variable-area recording.

The width of the clear portion of the track may be reduced considerably during periods of no sounds or weak sounds if, in the presence of louder sound, the width of the clear portion of the track is increased sufficiently so that the amplitude of the sound record does not exceed the width of the clear track. This is accomplished by adjusting the position of the illuminated triangle with respect to the slit so that when the modulation is zero, the apex of the triangle extends just beyond the slit opening. Thus, the negative receives a very narrow line of exposure along the middle of the track which, when developed to a negative and printed, results in the sound track shown in Figure 344b. As the modulation increases, the position of the triangle changes so that the mean position of its apex is farther and farther away from the slit opening. When the modulation is full, the distance between the slit opening and the mean position of the apex is equal to one-half of its maximum permissible excursion.

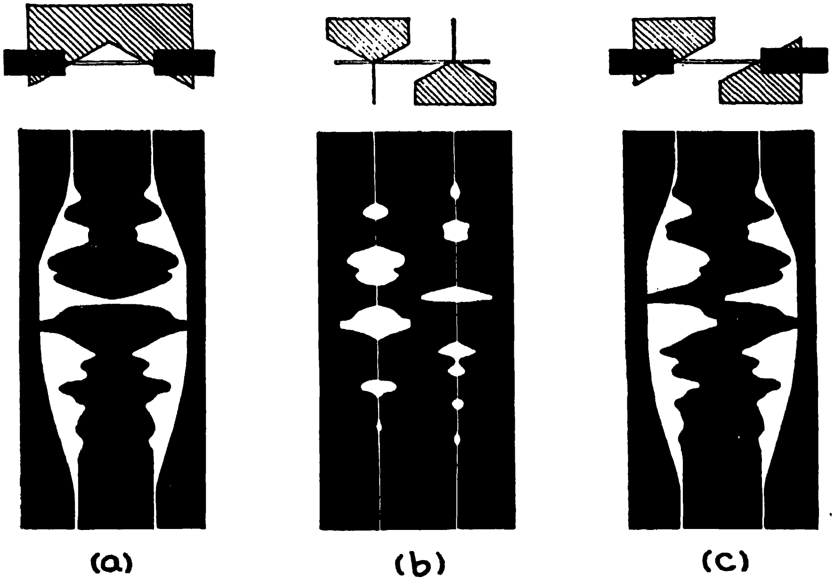

FIG. 346. Several types of variable-area sound tracks.

It is seen, therefore, that in normal recording the illuminated triangle, like the ribbons, has a constant average position; and its movement is essentially simple, corresponding to the variations of the voice currents only. In noiseless recording, however, the triangle may be regarded as having two motions: first, that due to the sound current only, as in normal recording; and, second, a superimposed, slower movement related to the envelope of these sound currents.

For the type of record shown in Figures 346a and 346c, the width of the clear portion of the track is controlled by an auxiliary galvanometer or shutter whose vanes are represented by the black rectangular areas. These are actuated by the low-frequency currents corresponding to the envelope of the sound currents and serve to mask off the unused portion of the light beam.

The type of track shown in Figure 346b requires no special noise-reduction system since it inherently possesses a higher signal to noise ratio than other known systems of film recording. It is not used extensively because of the necessity for maintaining an accurate balance of the two halves of the recording and scanning beams, the sensitivity of the two photoelectric cells, and the positioning of the tracks in the recorder [9a,10] and reproducer.

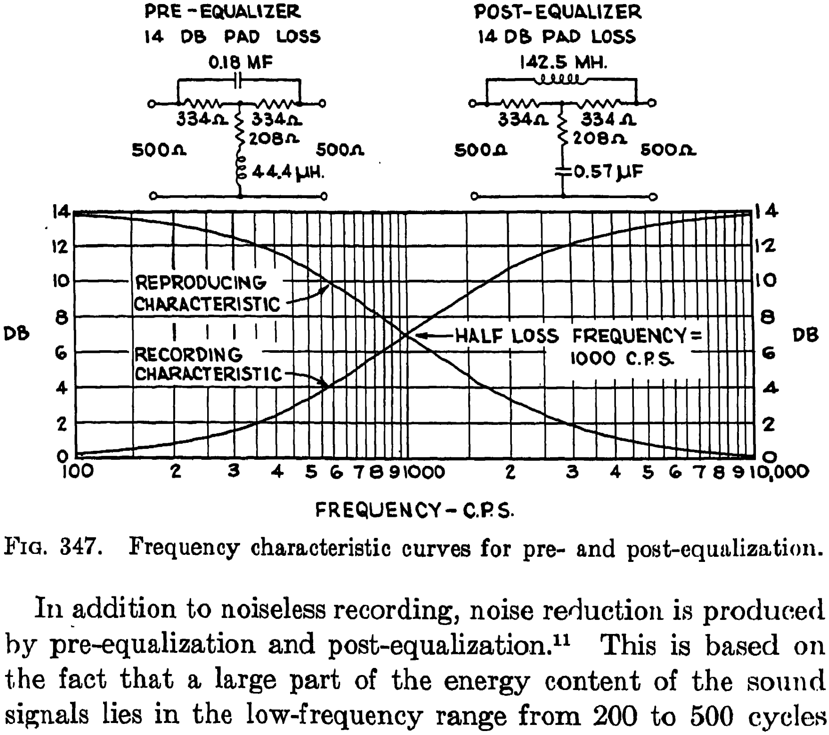

FIG. 347. Frequency characteristic curves for pre- and post-equalization.

In addition to noiseless recording, noise reduction is produced by pre-equalization and post-equalization.[11] This is based on the fact that a large part of the energy content of the sound signals lies in the low-frequency range from 200 to 500 cycles per second. An equalizer in the recording circuit, which decreases the low-frequency amplification with respect to the high-frequency amplification, distributes the signal load more uniformly upon the recording mechanism with respect to frequency. The channel gain can now be increased, a greater ratio of high-frequency signal to surface noise being thus obtained. By the introduction in the reproducing circuit of an equalizer having complementary characteristics, as shown in Figure 347, the frequency characteristic of the sound reproduced remains unchanged. Subsequent post-equalization, that is, reduction in the high-frequency amplification, reduces noise because the amplification of the high-frequency components in the noise is decreased correspondingly.

A further increase in the volume range of the reproduced sound is obtained by compression of the range of intensities of the original signals before they are recorded on the film.[11] This is accomplished by suitable electrical circuits associated with the recorder amplifier which control the amplification in a predetermined manner. The amount of compression is recorded on a separate track called the *pilot track* or the *control track*. By means of the control track and the necessary electrical circuits, the amplification of the reproducer amplifier is varied inversely to that of the recorder amplifier to restore the relative intensities of the signals to their original values.

2. The Reproduction of Frequency

Sounds occurring in nature,[12] such as speech, sound from musical instruments, and noises, contain components covering a wide range of frequencies. These various frequency components and their amplitude determine the character of the sounds. Theoretically, for the faithful reproduction of a sound, all the frequency components should be reproduced with the correct relative amplitudes. The loss in amplitude with frequency depends upon the resolving power of the emulsion and its use (Chapter XXI). The relative loss in the amplitude of different frequencies is usually called the *frequency characteristic*. It is determined by recording a series of frequencies at constant amplitude of the recording galvanometer and measuring the output level of the print at each frequency. The actual results of a set of such measurements, using commerically available emulsions, are shown in Figure 348 for a frequency range of 100 to 10,000 cycles per second. The output at 1000 c.p.s. is arbitrarily taken as the zero reference level.

In practice, the most satisfactory over-all frequency characteristics of the recording and reproducing systems are determined largely by the level of the background noise and waveform distortions. The background noise due to the granular structure of the photographic image is random in character, as is that due to numerous irregular scratches and small particles of dirt on the film surfaces. Thus, the level of the background noise is proportional to the width of the frequency band. The wave-form distortions are discussed in the next section.

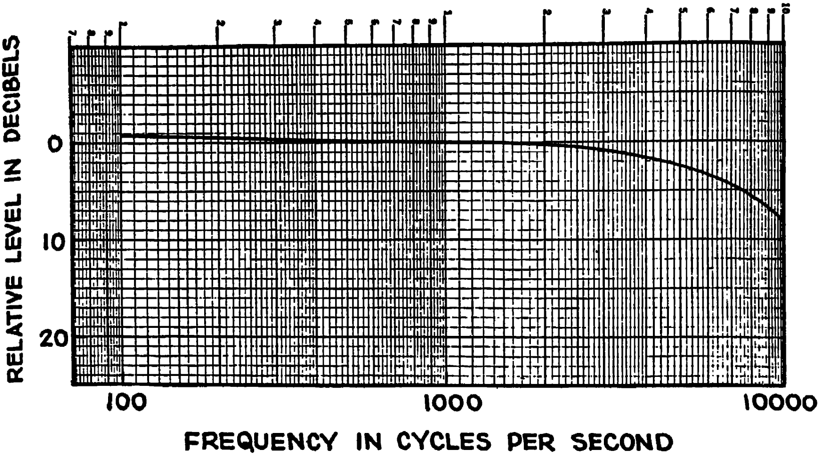

Fig. 348. Frequency characteristic curve.

3. The Reproduction of Wave Forms

For the original wave form to be retained, the transmission of the positive sound track must be linearly related to the exposure of the negative. The fulfillment of this condition for the variable-density and variable-area types of sound recording requires photographic materials of different sensitometric characteristics.[13] The variable-density method is considered first.

The effect of modifications in the photographic process—use of different film, different exposures, different developer or development time—can be computed from data on the sensitometric characteristics of the photographic materials. This was done some years ago by several workers;[14] but, in view of the complexity of the problem and the many conversion factors involved in these computations, it is better to determine the optimal sensitometric conditions by making a direct experimental study by methods closely related to commercial recording conditions. Then, the various conversion factors are included implicitly in the results and need not be evaluated. There are several methods for determining the wave-form distortions and the optimal sensitometric conditions. They deal with the overall characteristics and may embrace distortions not due to the photographic process, but the same principles apply.

If a simple sine wave is reproduced through a system with a nonlinear characteristic, the wave form is distorted; that is, it is no longer a simple sinusoidal wave. It is, however, periodic and, like any periodic function, can be expressed by a Fourier series of the form

$$\begin{aligned} y = a_0 + a_1 \cos x + a_2 \cos 2x + \cdots \\ + b_1 \sin x + b_2 \sin 2x + \cdots. \end{aligned}$$

In other words, if distortion is introduced into a simple sinusoidal function, additional components will be generated whose frequencies will be integral multiples of the fundamental frequency. These harmonics can be evaluated by Fourier analysis. The amplitude of the terms can be measured directly by means of an electrical frequency analyzer [15] or a mechanical analyzer operating on a microdensitometer trace of the wave form.[16]

The somewhat irregular curve in Figure 349 is a section of the microdensitometer trace of the sound record of a pure tone which, owing to wrong sensitometric conditions, had a large amount of harmonic distortion. The sinusoidal curve superimposed on the microdensitometer tracing represents the fundamental, and the curves below, the second to the sixth term, successively, in the Fourier series. The crosses represent the curve obtained by synthesis of the components shown. The close agreement between the original and the synthesized curve indicates that the composition of the wave is represented nearly perfectly by the first six terms. Actually, it is represented almost completely by the first four terms.

The photographic process in the cycle of sound reproduction depends upon the sensitometric characteristics of the emulsions used for the negative and the positive—that is, speed, grain size, and shape of the characteristic curve—and the physical characteristics of the developed photographic image—namely, resolving power, sharpness, turbidity, and granularity. It is evident that in the case of detail of microscopic dimensions, such as is the case when recording high-frequency components

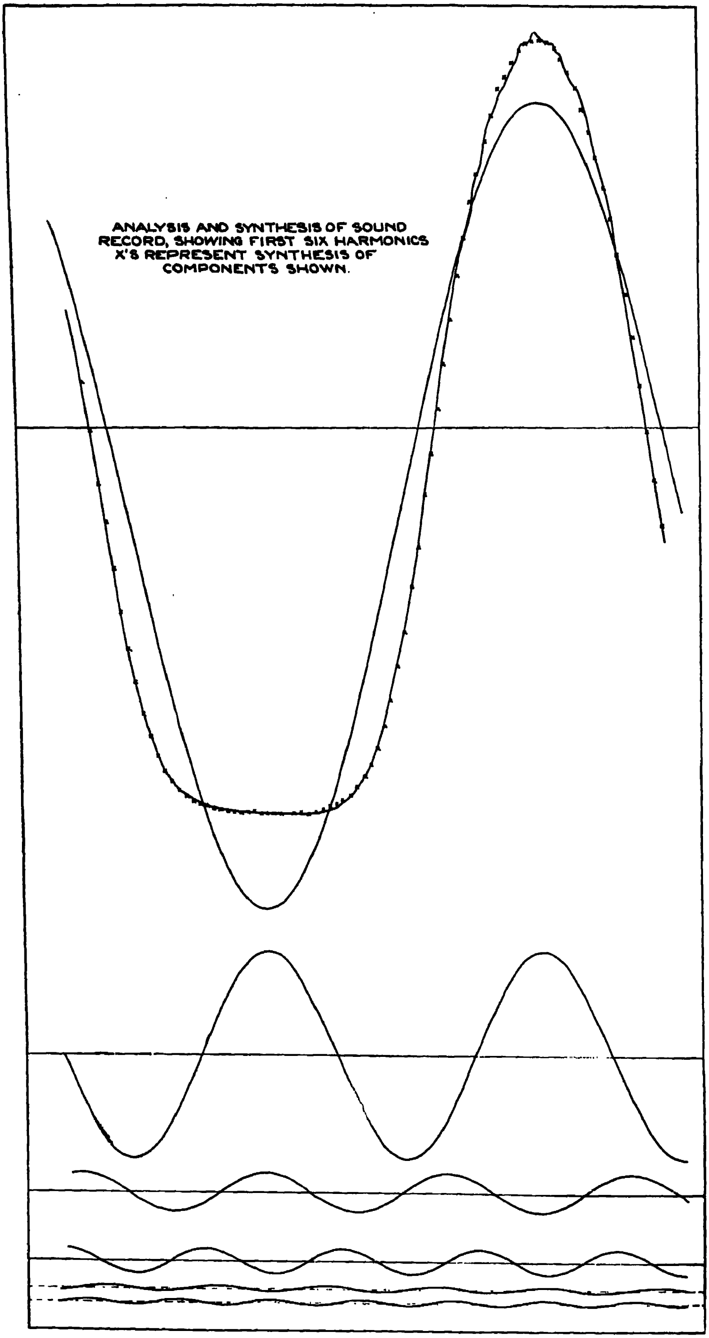

Fig. 349. Harmonic analysis and synthesis of sound record.

of sound, the reproduction of wave form cannot be predicted directly from the ordinary characteristic curves of a photographic emulsion obtained by exposing and measuring the density of relatively larger areas (Chapter XXI, p. 879). Nevertheless, the fundamental principles are the same, and much information can be obtained from a tone-reproduction diagram, such as that shown in Figure 350. Since the current of a photoelectric cell is linearly related to the transmission of the positive, it is convenient to use linear co-ordinates and plot transmission against exposure instead of density against the logarithm of exposure, as is customary in general photographic work. In quadrant I of the diagram, the transmission of the negative developed to a γ of 0.35 is plotted against the exposure. In quadrant II, the straight line is drawn at an angle which defines the exposure on the positive film in the printer. The characteristic curve of the positive film developed to a γ of 2.10 is plotted in quadrant III, the transmission being plotted against the exposure. Vertical lines for each exposure point in the negative in quadrant I meet horizontal lines drawn through the corresponding positive exposures on the positive curve in

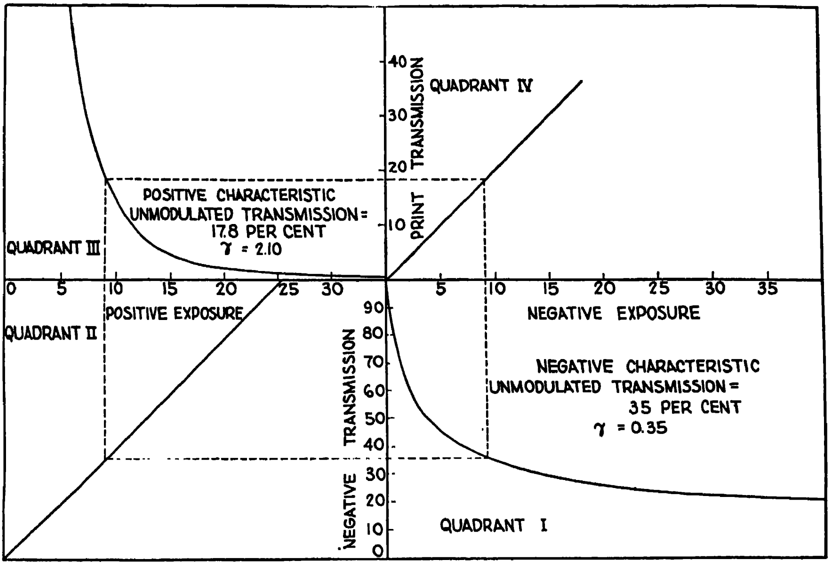

FIG. 350. Tone-reproduction diagram for sound recording.

quadrant III; and their intercepts trace the curve shown in quadrant IV, which represents the reproduction curve of the process. So far as this reproduction curve in quadrant IV is linear, undistorted reproduction should be obtained.

The application of this diagram to the reproduction of sound requires detailed consideration. In quadrant I, the exposure follows the axis from an average value indicated by the broken line and varies equally in the direction of increase and decrease. The average or unmodulated exposure results in average transmission, while the maximum and minimum values depend upon the modulation. For an arbitrary value of 9 as average exposure, the maximum modulation occurs when the light decreases to zero on the decreasing half of the cycle and increases to 18 on the increasing half. In terms of the light valve, this maximum means that the valve ribbons close completely, or clash, on the one hand, and open to double their average value, on the other. In terms of a glow lamp, the lamp is extinguished and has double its average intensity in the two halves of the cycle. In general, the amplification between the sound waves striking the microphone and the recording device is so adjusted that this maximum is reached only occasionally because the limits of the curve cannot be utilized without a considerable amount of distortion being introduced.

The straight line in quadrant II defines the positive exposure, which is proportional to the transmission of the negative, the coefficient of proportionality depending upon the intensity of the exposing lamp. Zero transmission of the negative always leads to zero exposure of the positive, so a family of straight lines through the origin represents all possible printing conditions.

Quadrant III shows the positive characteristic for a γ of 2.10.

Quadrant IV shows the final curve of positive transmission plotted against negative exposure. Since there is a straight-line relationship between positive transmission and negative exposure, and the photoelectric cell current in the reproducer is proportional to the transmission of the film, it follows that the photographic process is correct.

The diagram contains four variables; namely, the exposures of the negative and the positive, usually expressed in terms of unmodulated density, and the development of the negative and the positive expressed in terms of the γ's of the characteristic curves. The common commercial practice is to develop the negative and the positive print so that the *effective* product of their γ's is unity. For convenience, the degree of development of both the negative and the positive is determined from sensitometric strips exposed on a low-intensity sensitometer and measured on a diffuse-reading densitometer. Although this procedure is satisfactory for processing control, to determine the actual γ products in the sound tracks, certain conversion factors must be applied; hence, the term *effective γ product.* The application of these conversion factors is necessitated, for example, by the difference in γ of the high-intensity sound-track exposure and the low-intensity sensitometer exposure (Chapter VI), and the difference in γ based on diffuse densities and that based on specular densities measured by the photoelectric cell in the sound reproducer (Chapter XVII, p. 640). The γ's of the negative and the positive having been established, the two remaining variables are the unmodulated transmissions of the negative and the print, respectively. The characteristic curves of the

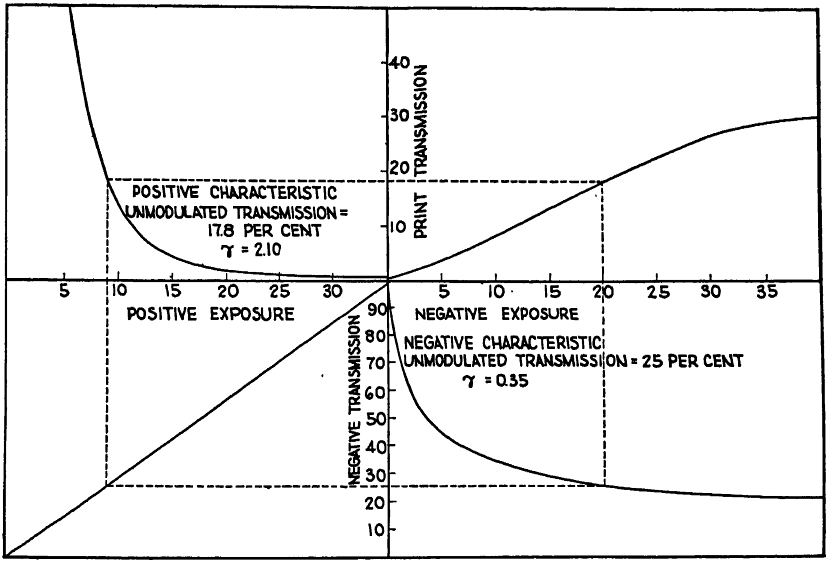

FIG. 351. Tone-reproduction diagram for sound recording with too low negative transmission.

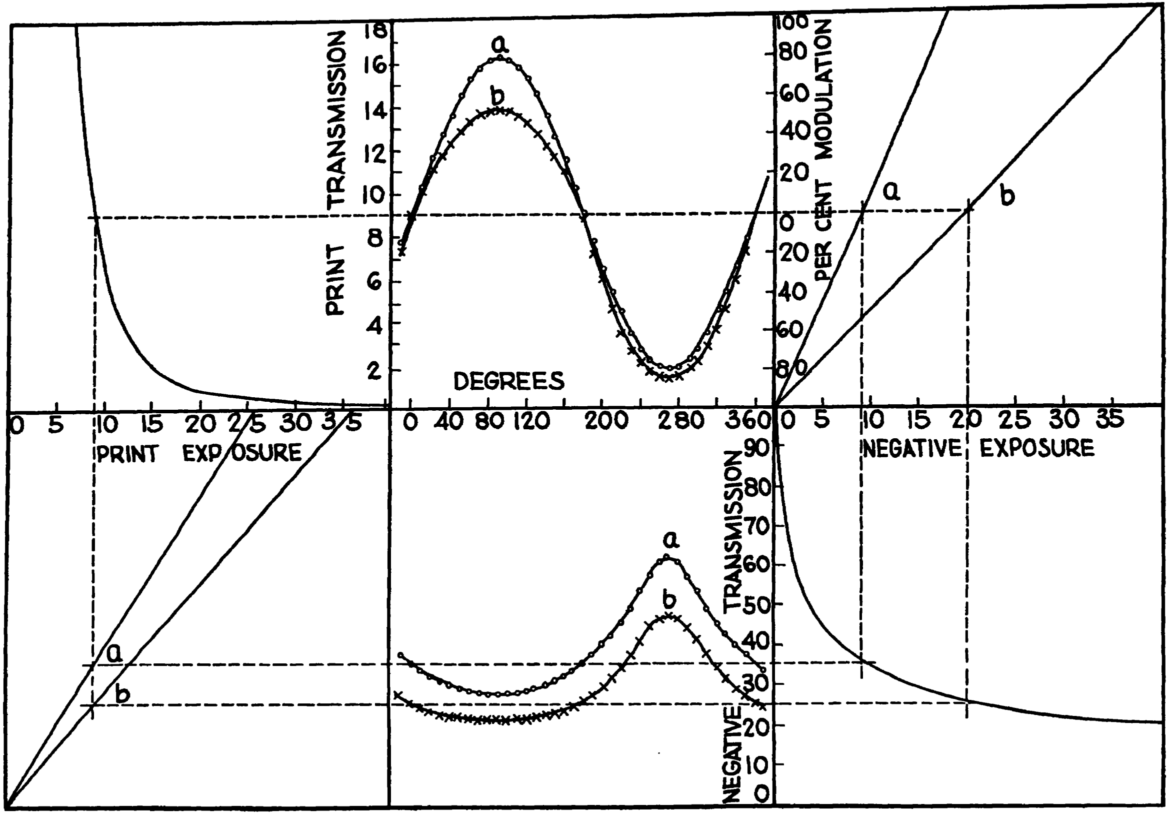

FIG. 352. Tone-reproduction diagram illustrating its application to the reproduction of a sinusoidal wave.

negative and the positive emulsions being known, the optimal operating points can be determined from the type of tone-reproduction diagram described above. In the case given, the unmodulated transmissions of the negative and the positive were 35 per cent and 17.8 per cent, respectively. By means of the tone-reproduction diagram also, it can be shown that a curvature can occur at either or both ends of the over-all curve in quadrant IV as a result of incorrect choice of negative and positive transmissions. Figure 351 illustrates the effect of too low negative transmission. A similar curve would result from operating at too high positive transmission, whereas too high negative transmission or too low positive transmission would produce a curvature at the other end of the over-all curve. This type of distortion can be greatly reduced by using push-pull recording. For this and other types of variable density tracks, the reader is referred to the original sources.[17]

The optimal sensitometric conditions can be determined by making a series of records of sinusoidal waves at several lamp currents and γ's, usually at two or three different frequencies. A series of positives at different printing exposures are made from each negative. The wave-form distortion of these prints is determined either by the method described previously, a recording microdensitometer being used to trace the wave form, which is analyzed by a mechanical harmonic analyzer or by an electrical frequency analyzer, which measures directly the amplitude of the terms in the Fourier series.

Figure 352 shows graphically the steps in the photographic sound-recording process applied to a sinusoidal wave. The cycle of operation begins in the top central compartment, where the curve *a* represents a simple sinusoidal current through the light valve. Two records are made using the modulation indicated by the reflection characteristics *a* and *b* in the upper right-hand compartment. The lamp current is adjusted so that the average negative exposures are 9 and 20 units, respectively, as shown in the lower right-hand compartment. The resultant negative wave forms are shown in the lower central compartment. By adjustment of the printer characteristic shown in the lower left-hand compartment to obtain for both records the same unmodulated print transmission shown in the upper left-hand compartment, the resultant wave forms for conditions *a* and *b* are represented by the circles and the crosses, respectively: *a*, corresponding to the sensitometric conditions in Figure 350, remains a simple sine wave; while *b*, corresponding to the conditions in Figure 351, is no longer a simple sine wave.

Another type of distortion that depends directly upon the harmonic distortion occurs in recording complex sounds, such as speech or music. This is known as *intermodulation,* or the modulation of the amplitude of one frequency component by another simultaneously impressed on the recording device. This distortion is encountered in variable-density records, particularly if a low-amplitude, high-frequency signal is impressed on a high-amplitude, low-frequency signal. Figure 353 is a microdensitometer tracing of a record of that type, where the low- and high-frequency components are 60 and 1000 cycles per second, respectively. Recalling Figures 349 and 352, it is seen that the average transmission of the 1000-cycle wave varies with the amplitude of the 60-cycle signal; thus, if a nonlinear relationship between negative exposure and print transmission exists, intermodulation will occur between the two frequencies. Two types of intermodulation distortion may be introduced by incorrect choice of negative or print exposure.[18] The first is shown in Figure 354, where, because of a choice of either too light a print or too dense a negative, the operation is too close to the shoulder of the over-all characteristic curve. A microdensitometer tracing of a sound record with this type of intermodulation is shown in Figure 355. A similar distortion would be obtained by excessive curvature in the toe owing to too dense a print or too light a negative or both. The second type of distortion is illustrated in Figure 356, where both negative and print exposures are too low, resulting in an over-all curve having excessive curvatures at both ends.

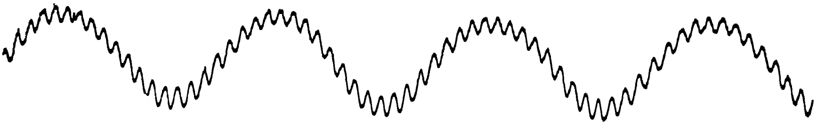

FIG. 353. Microdensitometer trace of film recorded with 60 cycles and 1000 cycles superimposed.

Figure 357 shows the wave shapes in successive stages of intermodulation measurements. Oscillogram *a* is similar to that in Figure 354 and is the result of nonlinearity at one end of the over-all characteristic curve. Thus, on the negative half of the low-frequency cycle, the amplitudes of the 1000-cycle loops are reduced compared to those on the positive half. This is more apparent in oscillogram *b*, where the 60-cycle signal has

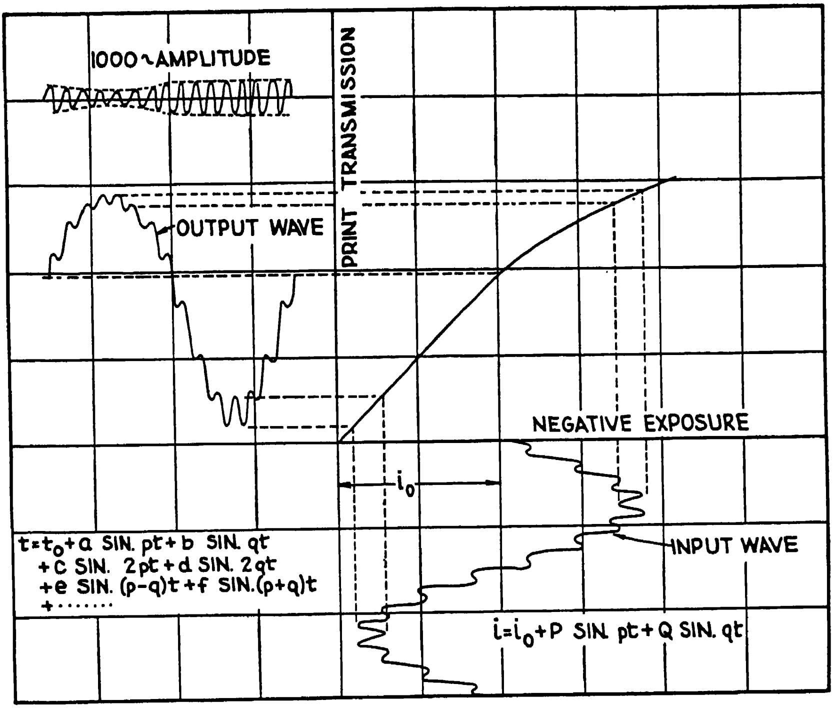
1000 ~ AMPLITUDE
PRINT TRANSMISSION
OUTPUT WAVE
NEGATIVE EXPOSURE
i_0
INPUT WAVE
$t = t_0 + a \sin pt + b \sin qt + c \sin 2pt + d \sin 2qt + e \sin (p-q)t + f \sin (p+q)t + \cdots$
$i = i_0 + P \sin pt + Q \sin qt$

Fig. 354. Analysis of intermodulation when nonlinearity exists at only one end of the film characteristic (test signal 60 and 1000 cycles superimposed).

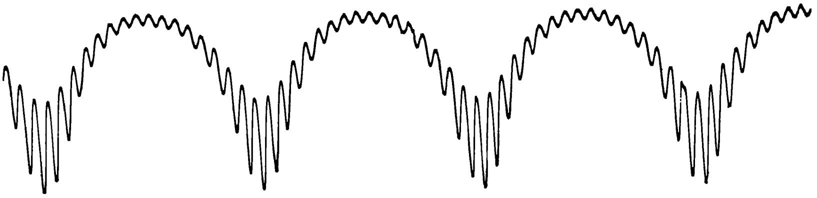

Fig. 355. Microdensitometer trace of the record whose analysis is shown in Figure 354.

been removed and the remainder amplified. Had there been no distortion, oscillogram *b* would have a constant amplitude. For the measurement of the percentage modulation of *b*, the wave is rectified as shown in *c* and passed through a 200-cycle low-pass filter, which removes the ripples and leaves a signal of the wave form shown in *d*. This signal is impressed on a transformer, which eliminates the direct-current component introduced by the rectification. The remaining alternating component is then measured on a volume indicator calibrated with reference to the average amplitudes, and the percentage of amplitude modulation ($R/S \times 100$) is indicated on a scale. The percentage of intermodulation is defined as the average deviation of the amplitude of the high-frequency wave from the mean value.

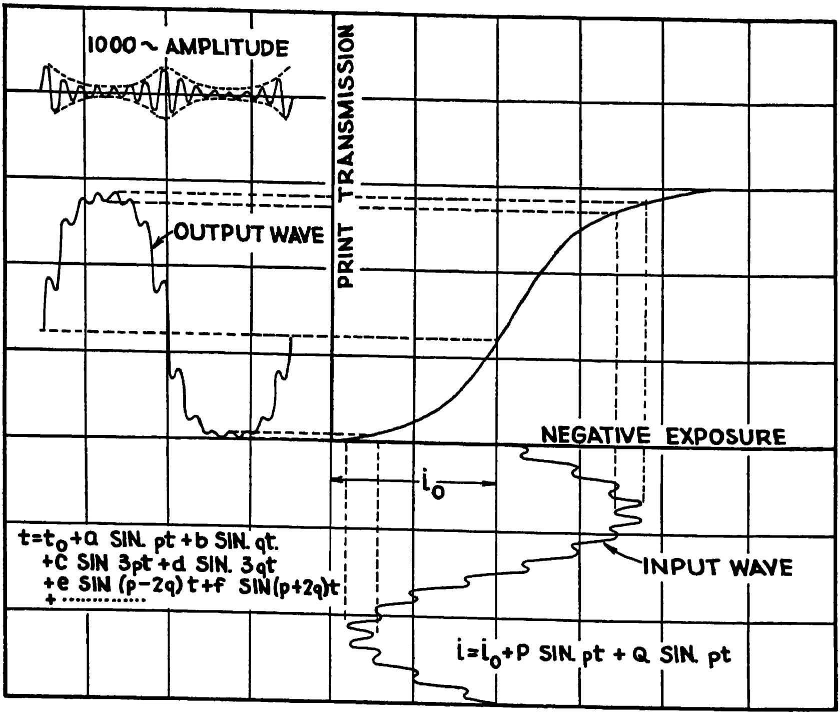

FIG. 356. Analysis of intermodulation when nonlinearity exists at both ends of the film characteristic (test signal 60 and 1000 cycles superimposed).

The mathematical relation between the readings of percentage modulation, as defined above, and percentage harmonic distortion can be derived provided certain assumptions are made as to the distortion process. For the first case, the assumption is that the distortion products are of the second order;

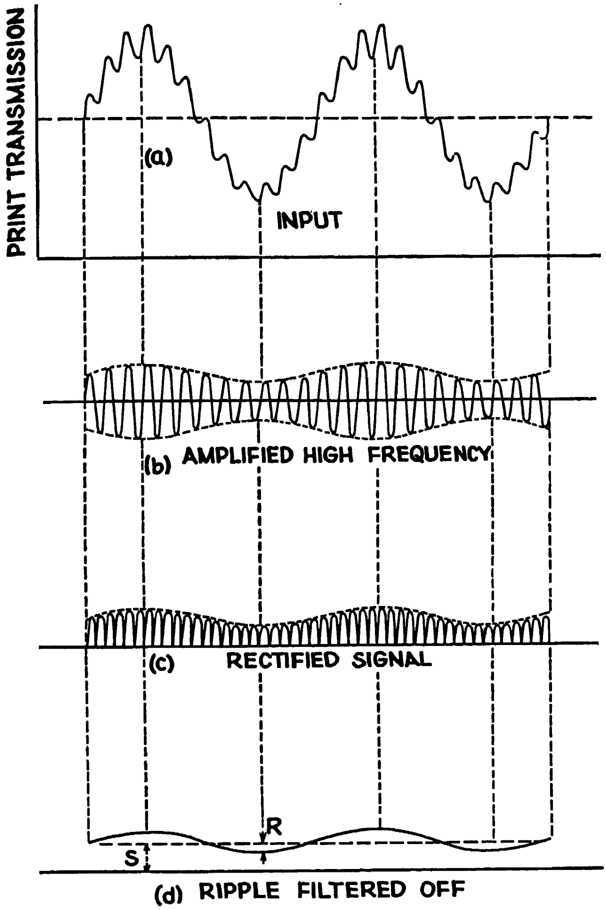

FIG. 357. Wave shapes in successive stages of intermodulation measurements.

that is, the output, y, has the following relation to the input current, x:

$$y = x + ax^2. \tag{1}$$

For the intermodulation test,

$$x = m_1 \sin \omega_1 t + m_2 \sin \omega_2 t, \tag{2}$$

where m_1 and m_2 are the amplitudes of the lower frequency ω_1

and the higher frequency ω_2, respectively. Substituting (2) in (1),

$$\begin{aligned} y = {} & m_1 \sin \omega_1 t + m_2 \sin \omega_2 t \\ & + a m_1^2 \sin^2 \omega_1 t + a m_2^2 \sin^2 \omega_2 t \\ & + 2 a m_1 m_2 (\sin \omega_1 t)(\sin \omega_2 t). \end{aligned} \tag{3}$$

The intermodulation tests measure the ratio

$$\frac{2 a m_1 m_2}{m_2} = 2 a m_1. \tag{4}$$

For the single-frequency harmonic test,

$$x = (m_1 + m_2) \sin \omega_1 t. \tag{5}$$

Substituting (5) in (1),

$$y = (m_1 + m_2) \sin \omega_1 t + a(m_1 + m_2)^2 \sin^2 \omega_1 t; \tag{6}$$

since

$$\cos 2x = 1 - 2 \sin^2 x,$$

equation (6) becomes

$$y = (m_1 + m_2) \sin \omega_1 t + \frac{a(m_1 + m_2)^2}{2} - \frac{a(m_1 + m_2)^2}{2} \cos 2\omega_1 t. \tag{7}$$

The ratio of the second harmonic to the fundamental is

$$= \frac{a(m_1 + m_2)}{2}. \tag{8}$$

The ratio of equation (4) to equation (8) expresses the relation of intermodulation to second harmonics and is

$$\frac{\text{Percentage intermodulation}}{\text{Percentage second harmonics}} = \frac{4 m_1}{m_1 + m_2}.$$

If the distortion products are of the third order, a similar expression can be derived for the relation between the percentage intermodulation and percentage distortion. In this case, the derivation is based on the assumption that the output, y, has the form

$$y = x + b x^3,$$

and the relation is

$$\frac{\text{Percentage intermodulation}}{\text{Percentage third harmonic}} = \frac{6m_1^2[4 + (3b)(m_1 + m_2)^2]}{(m_1 + m_2)^2(4 + 6bm_1^2)}.$$

If the distortion factor b is small, this will become

$$\frac{\text{Percentage intermodulation}}{\text{Percentage third harmonic}} = \frac{6m_1^2}{(m_1 + m_2)^2}.$$

Turning to the variable-area method of recording, it is seen that faithfulness of reproduction depends upon the reproduction of a geometric form. The optical system is so adjusted that when no sound reaches the microphone, a part of the sound track is illuminated to a fixed intensity, and the remainder of the track is unexposed. When sound strikes the microphone, the moving part of the recorder optical system—the galvanometer mirror—vibrates and varies the width of the illuminated portion of the track. The exposure of the fraction of the width of the track illuminated is at all times substantially constant.

The wave form of the recorded sound suffers a certain amount of distortion owing to lack of sharpness at the boundary of the exposed area and the change in the size of the photographic image with density. This lack of sharpness is due in part to scattered light in the optical system, a fraction of which reaches the section of the sound track lying outside the geometrical boundary of the image; partly to the finite size of the slit image; and partly to light scattered by the emulsion itself. The change in the size of the photographic image arises from two causes: One is the tanning of the gelatin by reaction products in the developer, which causes the image to contract; the other is the turbidity of the emulsion, which scatters the radiation, thus causing a growth in the size of the image with density (Chapter XXI, p. 907). The actual change in the image size depends upon both the size of the optical image and the density of the photographic image. Thus, for very small optical images, such as star images, the growth factor is large, whereas the contraction factor is almost negligible (Chapter XXI, p. 910). For images corresponding in size to individual wave lengths in the sound record, the effect of growth or contraction is greater, depending on the density and the frequency of the recorded waves. The difference in size of the optical and photographic images can be very large in the case of small optical images having high photographic densities. Hence, in a variable-area sound record, the image spread is more serious on high frequencies, as illustrated roughly by the photomicrograph of the parallel line resolving power test shown in Figure 358. The coarsest group of lines corresponds to a wave length in the mid-frequency range, while the fourth group corresponds approximately to that of the highest frequency. It is obvious that the difference in the size of the line and the space increases constantly as the spacing becomes smaller. The balance between the contraction of the image that occurs in the processing operations and its spreading—owing to the turbidity of the emulsion, the scatter of the light by the optical system, and other causes—falls at a density of about 0.75 for the type of emulsion used for sound recording. This density is too low to give a positive that is satisfactory from the standpoint of background noise; one which is satisfactory in this respect has a relatively large amount of wave-form distortion. However, this type of distortion in the negative can be largely removed by the proper choice of

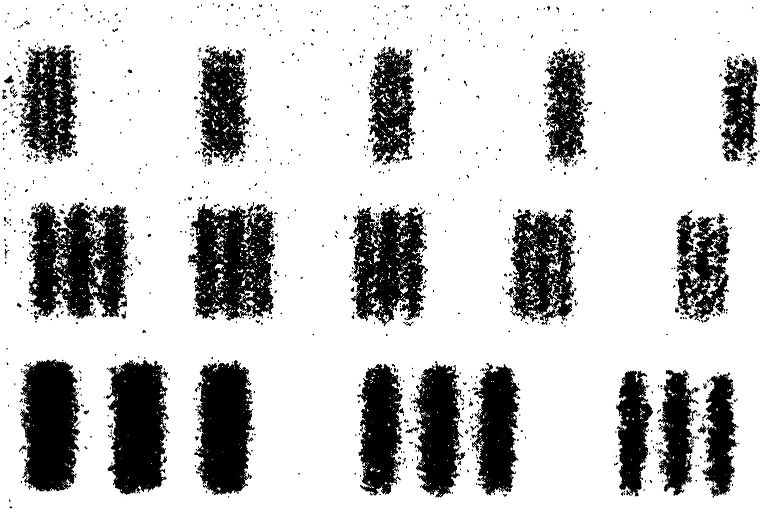

FIG. 358. Photomicrograph of a resolving power test on sound-recording film (×112).

print density; for each negative density, there is a print density which results in the minimum distortion. The print density that brings about the most complete cancellation of the distortion in a given negative is called the *cancellation density.*

The optimal sensitometric conditions—the correct exposure and development of the negative and positive variable-area sound record—have been studied by several investigators [19,14a] from both the theoretical and experimental standpoints. By experimental investigations,[20] using the method of harmonic analyses described above for variable density, the optimal sensitometric characteristics have been determined under practical working conditions. As in the case of variable-density recording, there are four variables; namely, the density and the γ of the negative and the print, respectively. The negative of the variable-area sound record is generally developed to a high γ to increase the sharpness of the edge of the exposed area. As in variable-density recording, the print γ is fixed by the picture requirements. It has been pointed out that the major cause of wave-form distortion in the negative is image spread, and that its magnitude is a function of the image density. The results of harmonic analyses have shown, however, that by proper choice of print density the distortion in the negative can be largely cancelled by the image spread in the print, which introduces a corresponding but complementary distortion. While the corresponding values of negative and positive densities can thus be determined by harmonic analyses, it is necessary when establishing their absolute values to take into consideration their relation to the signal to noise ratio and the frequency characteristic, because the best conditions for one are not necessarily the best for the others. For example, the density at which the waveform distortion in the negative is a minimum is too low to be satisfactory in regard to background noise. On the other hand, since the resolving power is a function of the image density (Chapter XXI, Fig. 325, p. 895), a very high sound-track density would seriously affect the frequency characteristic.

The conditions used at present are based on certain fundamental knowledge, substantiated by a vast amount of practical experience. The common practice is a print density between 1.30 and 1.40 on the film generally used for making motion-picture prints. The resolving power of the film is greatest in this density region. It is also considered the minimum density satisfactory from the standpoint of background noise. The corresponding cancellation density on the sound-recording negative emulsion is about 1.50 for "white light" recording—that is, unfiltered tungsten radiation—and about 2.00 for ultraviolet recording, using tungsten radiation transmitted through a nickel glass filter. The normal white light γ is generally between 2.30 and 2.50. It should be noted that in this case the control of density is of more importance than the control of γ and that within reasonable limits control of the latter is of importance only insofar as it serves as a processing control. The relation between print density at a γ of 2.00 and total harmonic distortion of a 4000 c.p.s. frequency is shown in Figure 359. The negative was made by using a tungsten lamp as a light source and recording on the type of emulsion used for the positive. The print cancellation density—the density at which the harmonic distortion is a minimum—is equal to the negative density. If the spreading of the image in the negative were reduced by change to a more contrasty emulsion, for example, or by the use of ultraviolet radiation, its density would have to be increased to re-establish its complementary relation to that of the positive. This is shown later in a description of another method of determining the distortion in variable-area sound records.

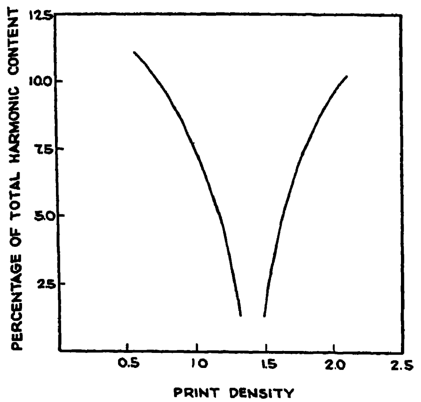

Fig. 359. Harmonic distortion in a 4000-cycle per second record as a function of the print density.

Ultraviolet radiation is used quite generally for variable-area sound recording.[21] The primary reason is the increase obtainable in the sharpness and the resolving power of a normal photographic emulsion.[22] This is due to the increased absorbing power of the emulsion for the shorter waves, the photographic image being thus confined to the surface and thereby effectively decreasing the image spread. Other means for concentrating the image near the surface also increase the resolving power and the sharpness.

Two methods based on the use of two signal frequencies have been developed for measuring distortion in variable-area sound records.[23] They differ in that in one, two sinusoidal waves of several thousand cycles are recorded simultaneously and the amplitude of the modulation products generated as a result of nonlinearity in the photographic process is measured; in the other, an amplitude-modulated high-frequency sine wave is recorded and the demodulation products are measured.

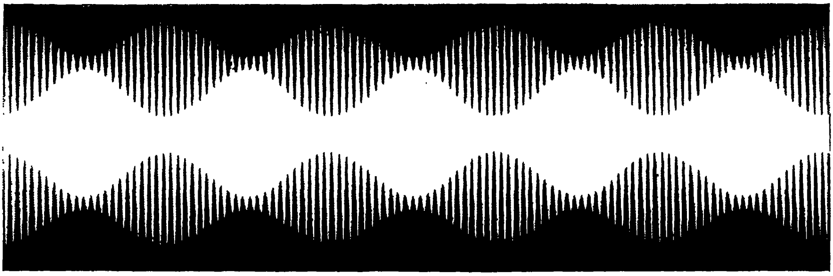

FIG. 360. Photomicrograph of film recorded with 9000 cycles amplitude modulated with 400 cycles.

The latter method, known as the *cross-modulation method,* may be described in some detail. A high-frequency signal of 9000 cycles, say, is modulated 75 per cent by a low-frequency sine wave of 400 c.p.s. After modulation, the low-frequency signal is removed by a high-pass filter in the electrical circuit, and the remaining amplitude-modulated high-frequency signal is recorded on the film. A photomicrograph of such a record is shown in Figure 360. From analogy with the parallel line test object, it is evident that the area of the developed photographic image representing the 9000-cycle wave is smaller or larger than the area exposed, depending upon the density and amplitude of the signal, with a corresponding change in the average transmission of the sound track. In other words, if the sensitometric conditions are not correct; that is, if the system is nonlinear, a 400-cycle component will appear as a result of the demodulation or rectification action in the photographic process. This is illustrated further by the diagrammatical representation in Figure 361 of records of simple sine waves that have undergone distortion owing to overexposure. The top and middle diagrams illustrate that the change in the average transmission, indicated by the dotted line, increases with the amplitude; while the bottom diagram shows how a new frequency is introduced by virtue of the wave train. The increase or decrease in the average transmission of the modulated exposure compared to the unmodulated exposure is also called *zero shift.* It can be determined by comparing the transmission of an unmodulated section of track with a section of equal length modulated by the high frequency selected for testing. The comparison can be made either by a photometer that measures the total light flux through a rectangular aperture used to limit the section of sound track or by a microdensitometer. Figure 362 is a record obtained by the latter method, showing the zero shift for two different types

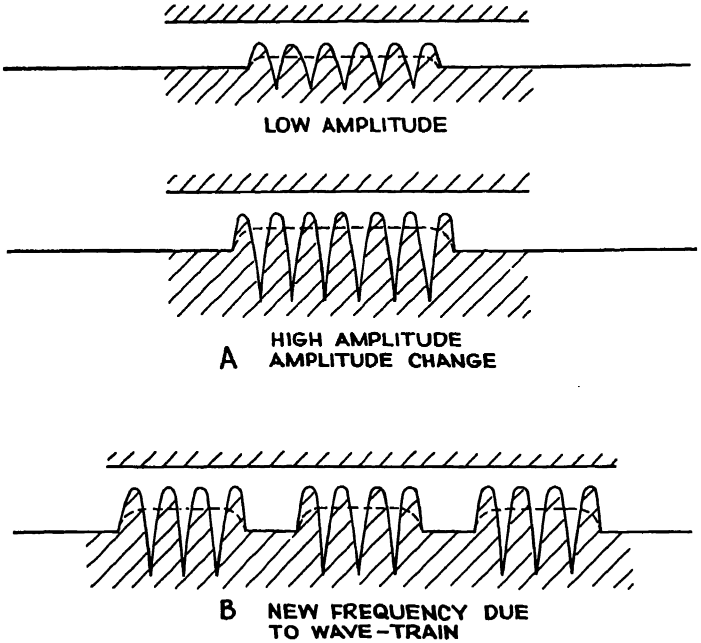

Fig. 361. Distorted sine waves. *A* illustrates the change in average transmission with amplitude; and *B*, the introduction of new frequencies owing to the wave train.

of emulsions. It is interesting to note that, although the maximum densities in the two tracks were the same, the zero shift in *a* is much greater than that in *b*.

From the preceding discussion, it becomes evident that if the record of the type of wave shown in Figure 360 is either underexposed or overexposed, at least one new frequency, namely 400 c.p.s., will be introduced as a result of demodulation. This demodulation component can be measured by inserting a 400-cycle band pass filter in the reproducer amplifier circuit, which removes not only the 9000-cycle signal but also most of the background noise. The removal of the noise is necessary because the level of the 400-cycle demodulation signal approaches the noise level as the sensitometric conditions approach optimal. To determine the optimal sensitometric conditions, recordings of equal peak amplitudes are made of 1000- and 9000-cycle notes, and a 9000-cycle note is modulated 75 per cent by a 400-cycle note. These recordings are made at several values of exposure, and a series of positives from each negative is made at different printing exposures and processed in the normal manner. The amplitude of each frequency should be adjusted by a known and fixed amount below 100 per cent of the galvanometer swing.

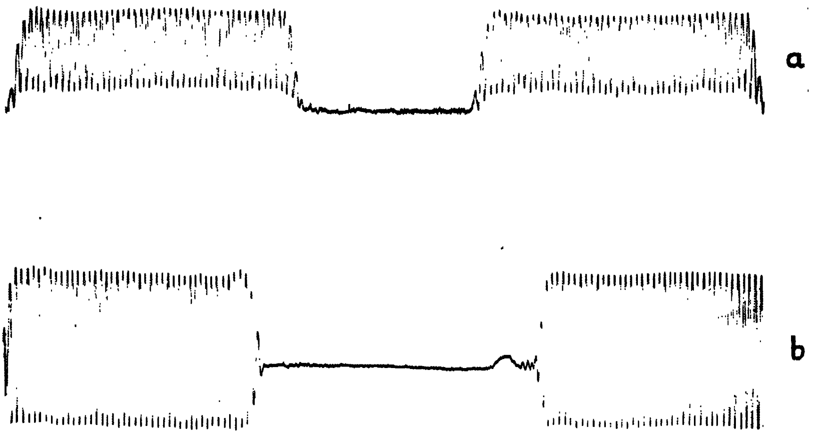

FIG. 362. Microdensitometer trace of 9000-cycle record showing zero shift on two different types of emulsions.

To provide a uniform method for comparison purposes, the output readings must be corrected for all losses in the measuring circuit, such as filter attenuation, amplifier response, and *scanning slit loss*.[24] The 400-cycle output must also be referred to 100 per cent modulation. All the corrected output readings are then compared to the maximum output of 1000 cycles, as the reference level.

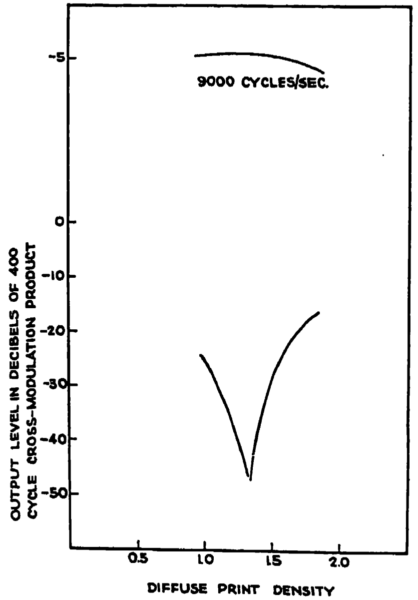

FIG. 363. Cross-modulation products in decibels as a function of the print density.

The results of a set of measurements are shown in Figure 363, where the level of the cross-modulation products in decibels below the level of the 1000-cycle note is plotted against the print density. This series of prints was made on standard motion-picture positive film from an ultraviolet negative of density 2.00 and white-light control γ of 2.50. The distortion approaches a minimum at a density of about 1.30, bearing out an earlier statement that as the image spread in the negative is diminished, its density with respect to that of the print must be increased.

The relation between the cross-modulation products and harmonic distortion can be derived by a method similar to that used for variable-density intermodulation tests provided the same assumptions are valid for the distortion process; namely, that the photographic process causes a second-order distortion, so that the output is related to the input current, x, as follows:

$$y = a_0 + a_1x + a_2x^2. \tag{1}$$

The input current, that is, the modulated signal recorded on the film, is

$$x = m_2 \sin \omega_2 t + mm_2 \sin \omega_1 t \sin \omega_2 t, \tag{2}$$

where m_2 is the maximum amplitude of the unmodulated carrier signal whose frequency is ω_2 and m is the modulation of the carrier by the signal whose frequency is ω_1. Substituting equation (2) in (1) and omitting all terms but the square term, that is, the term contributing to the second-order distortion component, y_1:

$$y_1 = a_2 m_2^2 \sin^2 \omega_2 t + a_2 m^2 m_2^2 \sin^2 \omega_1 t \sin^2 \omega_2 t + 2a_2 m m_2^2 \sin \omega_1 t \sin^2 \omega_2 t. \quad (3)$$

The method of measuring cross-modulation products just described makes use of only the components whose frequency is ω_1. Only the third term in equation (3) can produce ω_1 components. This term reduces to

$$a_2 m m_2^2 \sin \omega_1 t - a_2 m m_2^2 \sin \omega_1 t \cos 2\omega_2 t, \quad (4)$$

of which the first term is measured. The measurement is the ratio of the ω_1 component to the amplitude of a sinusoidal wave having approximately the same peak amplitude as equation (2) or

$$\text{cross-modulation ratio} = \frac{a_2 m m_2^2}{m_2 + m m_2} = \frac{a_2 m m_2}{1 + m}. \quad (5)$$

For the single-frequency harmonic test,

$$x' = (m_2 + m m_2) \cos \omega_2 t. \quad (6)$$

Substituting (6) in equation (1), the distortion component, y'_1, is

$$y'_1 = a_2 (m_2 + m m_2)^2 \cos^2 \omega_2 t = \frac{a_2}{2} (m_2 + m m_2)^2 + \frac{a_2}{2} (m_2 + m m_2)^2 \cos 2\omega_2 t. \quad (7)$$

The ratio of the second-harmonic component to the fundamental is

$$\frac{a_2 (m_2 + m m_2)^2}{2(m_2 + m m_2)} = \frac{a_2 (m_2 + m m_2)}{2}. \quad (8)$$

The ratio of cross-modulation products to second-harmonic distortion is given by the ratio of equation (5) to (8) and is

$$\frac{a_2 m m_2}{1 + m} \cdot \frac{2}{a_2 m_2 (1 + m)} = \frac{2m}{(1 + m)^2}. \quad (9)$$

For the usual value of m of 0.75, the ratio of cross-modulation products to harmonic distortion is 0.49. While the photographic process may produce third-order distortion components, their derivation is not considered here, because the products are of frequencies which are not measured in the usual cross-modulation test. Equation (7) contains a rectified component, $\frac{a_2}{2}(m_2 + mm_2)^2$, which is related to the cross-modulation products, and has already been suggested as a simple means of determining the optimal processing conditions. This method, known as zero shift, was discussed in connection with Figure 362.

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PART VI

OPTICAL SENSITIZING

CHAPTER XXIII

SPECTRAL SENSITIVITY

The action of the solar spectrum upon silver chloride was first studied in 1777 by Scheele, who noticed that blackening was much more rapidly produced by violet light than by light of other colors. Scheele's results were confirmed by Senebier in 1782, and by projecting the spectrum upon silver chloride Ritter discovered the ultraviolet in 1801, this discovery being made almost simultaneously by Wollaston in 1802. Wollaston drew attention to the fact that the more refrangible radiations were chemically the most active and called them chemical radiations.

The spectral sensitivity of photographic materials is governed by their absorption, in accordance with Grotthus' law.* Thus, silver chloride, which is almost colorless, is sensitive only to ultraviolet and extreme violet. Silver bromide, which is pale yellow, is sensitive well into the blue.

The spectral sensitivity and spectral absorption curves of emulsions made with pure silver chloride and silver bromide, and also of a bromo-iodide emulsion, are shown in Figure 364. The spectral absorptions were determined with an automatic spectrophotometer of the Hardy type. The values of total reflectance and transmittance in diffuse illumination were added and the sum subtracted from 100 per cent. Illumination of the sample by dispersed light and rapid operation reduced blackening of the emulsion to a minimum; and the sum of reflectance and transmittance in the longer wave lengths was 96 per cent or higher, so that this method can be assumed to measure the true absorption with reasonable accuracy in spite of the scatter by the sample. The sensitivity curves were obtained by exposure in a monochromatic sensitometer of the general type first described by Jones and Sandvik.[1] Sensitivity is expressed as the inverse of the incident energy of a given wave length necessary to produce a density of unity. Agreement between the absorption and sensitivity curves is adequate. Maximum sensitivity is reached at an absorption of 60 to 70 per cent. This would have been altered appreciably by choice of another density for measurement of sensitivity. At a density of unity, not more than one fourth of the silver halide has been reduced, and this is principally in the upper part of the emulsion. Further increase in total absorption confines the effective exposure to a thinner and thinner layer in which the proportion of grains developable increases quite slowly with exposure, so that the change in sensitivity with absorption becomes correspondingly small. Mixtures of silver chloride and bromide have sensitivities intermediate between those of the single halides.

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* This law was rediscovered by Draper in 1841 and enunciated by him as follows: "The chemical action produced by the rays of light depends on the absorption of these rays by sensitive bodies."

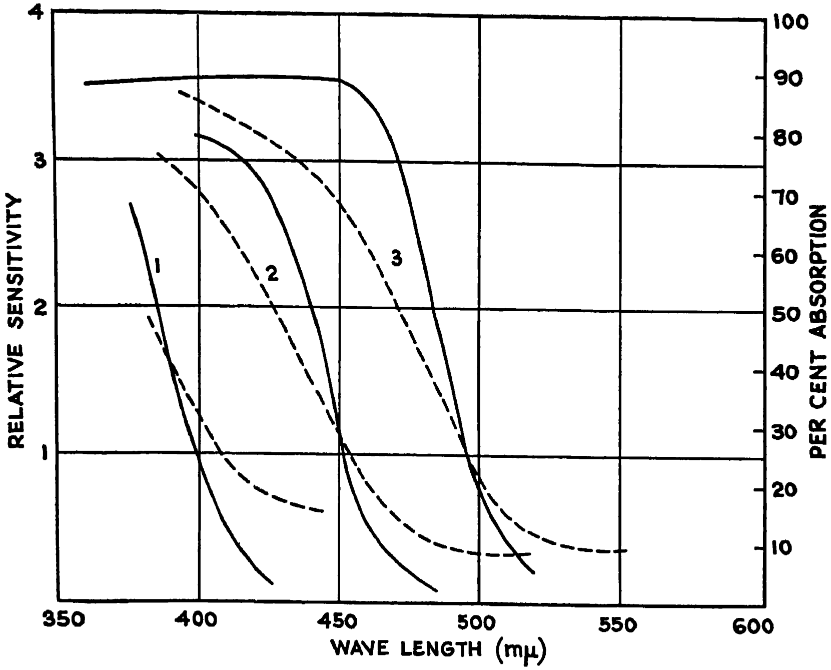

Fig. 364. Spectral sensitivity and absorption curves of (1) pure silver chloride emulsion, (2) pure silver bromide emulsion, and (3) silver bromoiodide emulsion—5½ mol per cent silver iodide: *solid line*, sensitivity; *broken line*, absorption.

The absorption curve of a very fine-grained dispersion of silver iodide in gelatin is given in Figure 365. The photographic sensitivity is too low to be measured in a monochromatic sensitometer; but wedge spectrograms of silver iodide, both as a gelatin emulsion and as collodion wet plate, are given by Huse and Meulendyke.[2] These show a maximum at 420 mμ corresponding to the peak of absorption at the same point. Most practical emulsions are made with silver bromide containing small amounts of iodide. Their absorption and sensitivity do not fall between those of emulsions made with pure bromide and iodide. The color of mixtures containing more than one per cent of iodide is deeper than that of silver iodide. Wilsey [3] showed that if silver bromide and iodide are fused together, the mixed crystals have the simple cubic lattice characteristic of silver bromide up to about forty mol per cent iodide, but the spacing of the lattice becomes greater with increasing

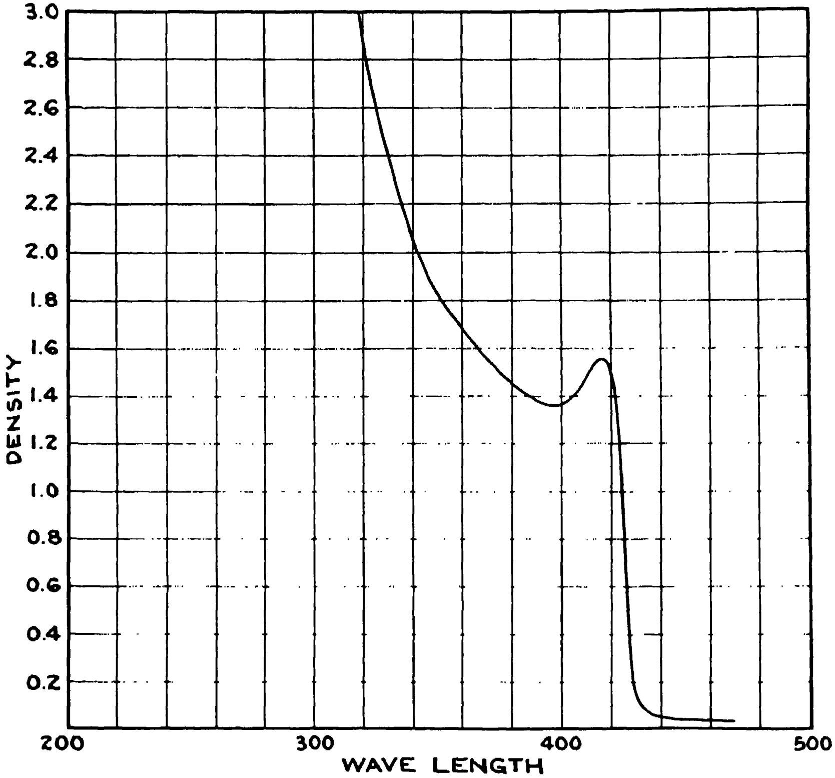

FIG. 365. Absorption curve of fine-grained silver iodide in gelatin.

proportion of iodide. At about thirty per cent, the hexagonal lattice of silver iodide appears (Chapter I, p. 30). Huse and Meulendyke prepared emulsions with increasing amounts of iodide and found that up to thirty mol per cent the color became deeper and the sensitivity extended to longer wave lengths.

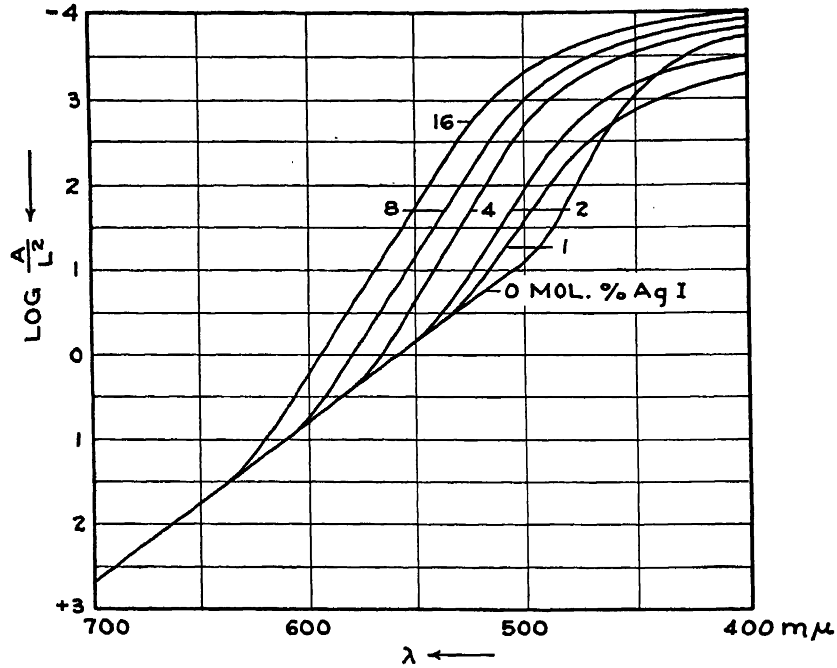

FIG. 366. Spectral sensitivity curves of silver bromide containing varying proportions of silver iodide. (In Figs. 366–369, the sensitivity is expressed as the logarithm of the ergs per square cm. required to produce, after development, a density of 0.1 above the fog density.)

At thirty-two mol per cent, the characteristic sensitivity maximum of silver iodide appeared at 420 mμ, indicating that the limit of stable mixed crystals is between thirty and forty per cent. Spectral sensitivity curves of silver bromide containing varying proportions of silver iodide are given in Figure 366, taken from a paper by Eggert and Biltz.[4] The maximum sensitivity of silver bromo-iodide lies well into the ultraviolet, but the effective maximum of an emulsion in gelatin was found by Jones and Sandvik to be close to 350 mμ because of the absorption of gelatin. This begins in the violet and increases with decreasing wave length. At about 200 mμ it is so strong that the sensitivity of an ordinary emulsion disappears, to reappear in the X-ray region. Other colloids have different absorptions, but none is adequately transparent below 250 mμ. For photography of the far ultraviolet, it is necessary to use emulsions very low in gelatin (Schumann plates) or ordinary emulsions coated with fluorescent materials.

Eggert and his collaborators [5] have studied the sensitivity of unsensitized emulsions in detail. Their data show that the sensitivity of silver bromide is proportional to its absorption of light, so that the decrease in sensitivity with increasing wave length is caused by decrease in absorption only and not by a decrease in intrinsic sensitivity. In Figure 367, taken from Eggert and Kleinschrodt, the logarithm of sensitivity of a colloid-free silver bromide coating is plotted against the extinction coefficient calculated from the measurements of Slade and Toy and of Hilsch and Pohl; the change in slope from 400 to 420 mμ is caused by the lack of proportionality between extinction coefficient and absorption as the absorption becomes stronger.

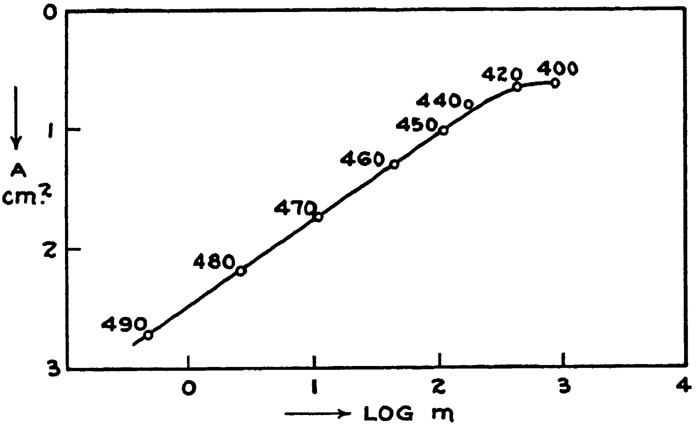

Fig. 367. Relation between the sensitivity of a colloid-free silver bromide coating and its extinction coefficient for light.

When the measurements in Eggert's laboratory were extended to longer wave lengths, it was found that the spectral sensitivity curve of pure silver bromide emulsions has a break at about 500 mμ, as shown in Figure 368. Eggert suggests that at this point the absorption of light by impurities and breaks in the crystal lattice (the "electron traps" of Gurney and Mott) come into play. When the emulsion contains silver iodide, the break in the curve occurs at a longer wave length, depending on the proportion of iodide present (Figure 366). The curves for all proportions of iodide appear to join the curve for pure bromide, indicating that the iodide has acted as an optical sensitizer. The effect of dye sensitizing is similar to that of iodide.

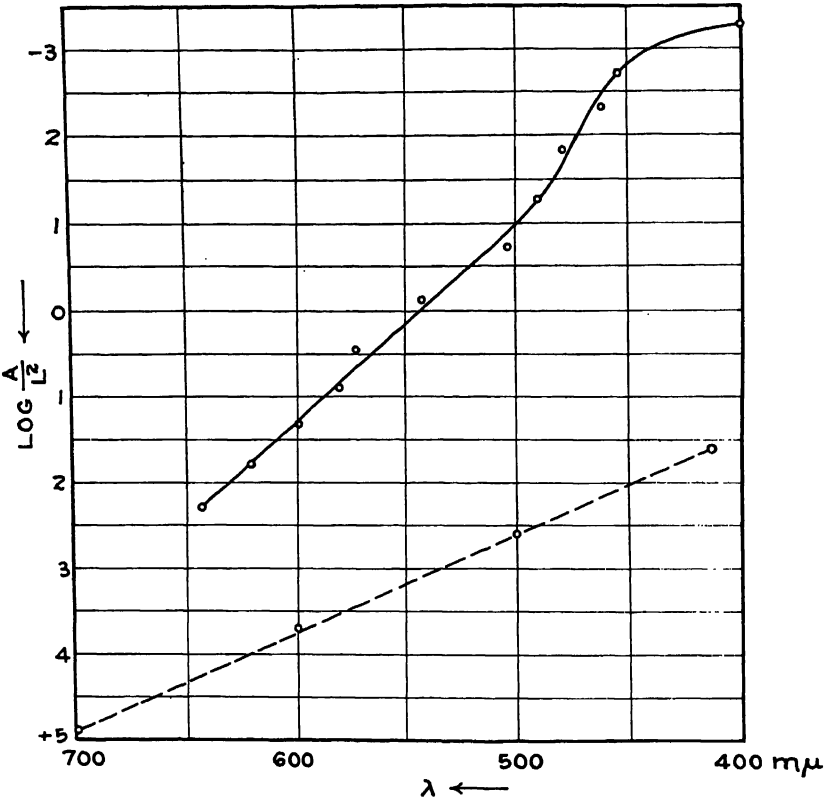

FIG. 368. Spectral sensitivity of a pure bromide emulsion for the longer wave lengths. *Solid line,* developed image; *broken line,* visible image produced by light.

Eggert and Kleinschrodt studied the spectral sensitivity of unsensitized emulsions in relation to the protective colloid and method of preparation. Their results are summarized in

Figure 369. The break in the curve at about 500 mμ was observed in every case except that of colloid-free silver bromide. The slope of the curve past 500 mμ decreased with increased ripening of the emulsion, as would be expected if it is caused by the chemical products of the process. The break in the curve occurred even when collodion and hydrated cellulose replaced gelatin. The extent of the break depended on the type of gelatin and the emulsion formula; it almost disappeared on using a special inert gelatin. These data are consistent with the hypothesis that sensitivity in the region past 500 mμ depends on absorption by specks of foreign material in the structure of the silver bromide grains. From 650 to 750 mμ, sensitivity again decreased more rapidly.

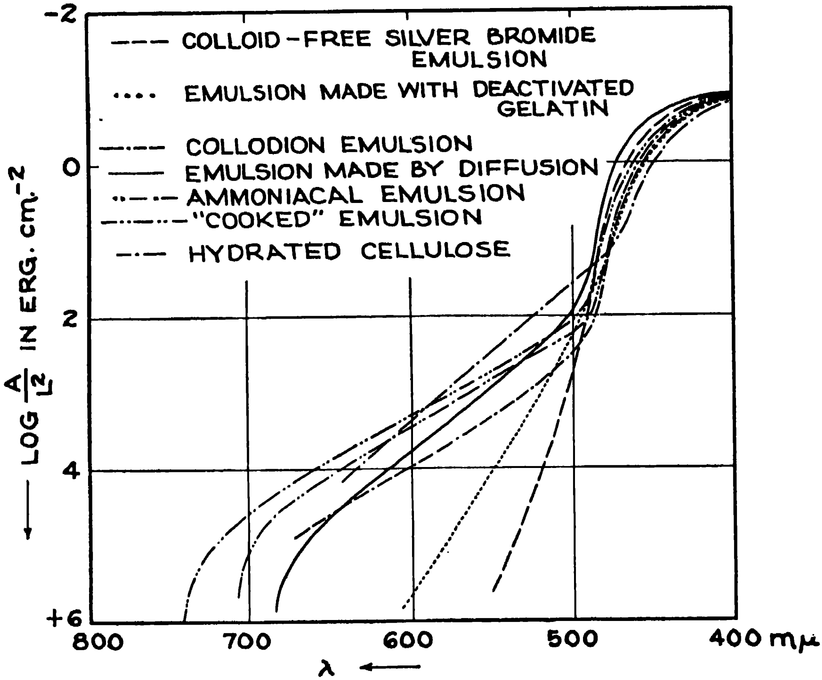

FIG. 369. Spectral sensitivity of emulsions made with various dispersing agents, plotted to give equal sensitivity at λ 400 mμ.

The sensitivity of silver halides for wave lengths greater than 500 mμ is negligible for practical purposes, and the spectral absorption of the emulsion must be extended if it is to be used for this region. This is done by means of dyes in the usual process of optical sensitization, but other means not clearly understood were discovered and used in the early days of the art. Abney [6] prepared a special collodion emulsion by digestion with an excess of silver salts. It was blue by transmitted light and sensitive throughout the visible spectrum and well into the infrared. With this material, he photographed the solar spectrum to 1075 mμ. Abney's preparation was successfully repeated by Ritz,[7] although other investigators have failed. A similar (although lesser) extension of sensitivity in gelatin emulsions was observed by Capstaff and Bullock [8] in gelatin emulsion plates which had been bathed in dilute solutions of bisulfites, followed by a prolonged wash in faintly alkaline water. Neither of these methods is of use in practice. It is believed that both are forms of sensitization by colloidal silver. Sensitization for photolysis by the silver first formed was observed by Becquerel [9] in the early days of photography and studied quantitatively by Weigert.[10] There is no direct evidence of sensitization by colloidal silver for latent-image formation; but Wightman, Trivelli, and Sheppard [11] demonstrated the marked sensitivity of photohalides for longer wave lengths. Silver sulfide may act both as an optical sensitizer and a chemical sensitizer.[12]

Sheppard [13] reviewed the subject of optical sensitization by silver and silver sulfide and concluded that it "is primarily due to sensitized photoelectric emission by silver amicrons and ultramicrons." Other minor effects are known, such as the sensitization produced in some emulsions by bathing with dilute solutions of iodide or cyanide.[14]

SENSITIZING BY DYES

The discovery that the addition of a dye to a silver bromide emulsion confers sensitivity to the portion of the spectrum absorbed by the dye was made in 1873 by Vogel.

While investigating some collodion dry plates, he noticed that upon exposure to the solar spectrum they showed some sensitivity in the green, and he found that this unusual sensitivity was due to the presence in the plate of a yellow dye which had been added to prevent halation.[15] Vogel sought to reproduce the effect by impregnating a silver bromide plate with a dye which absorbed green light. He chose coralline and found that the plates behaved as he had hoped. The experiment was modified by the use of dyes which absorbed red, and among the green aniline dyes were found some which absorbed red strongly, one of which sensitized emulsions to the red portion of the spectrum.

It was clear to Vogel that he had discovered a phenomenon of the greatest significance, and he himself says:

> "It may be assumed with considerable certainty that we are in the position to render silver bromide emulsions sensitive to any desired color as well as to increase the normal sensitiveness to certain colors. It is only necessary to add a substance which promotes the decomposition of the silver bromide and which absorbs the desired colors and not the others. Perhaps it will be possible to photograph the infrared in the same way as the ultraviolet. . . . It had previously been supposed that the silver halides were only altered by the rays that they absorbed (Schultz-Sellack, *Ber.*, 4, 211; 1871) . . . the above work shows that not only the absorption of the halides but the absorption of substances mixed with them is significant."

Vogel's discovery excited considerable attention, although at first a number of investigators attempted to repeat his experiments without success.[16] But others supported them,[17] and it gradually became known that for the effect to be clearly observed, the dye should be very pure and used in rather high dilution, conditions that were probably not fulfilled in much of the early work.

However, all dyes do not possess sensitizing action, and many give rise to side effects which spoil the emulsions. Even with dyes considered most suitable, Vogel himself obtained only one good plate to five bad ones, and under these conditions the process could not be introduced commercially. At about this time, gelatin dry plates were coming into use; and with them *optical sensitizers*, as they came to be known, gave such poor results that Vogel regarded this as characteristic of this type of material.

In spite of early discouragement, however, optical sensitizers were adopted, the first commercial use being made in France, where in 1875 Ducos du Hauron and C. Cros used coralline for preparing green-sensitive plates for color photography and chlorophyll for red-sensitive, this material having been found by Becquerel[17c] to be a red sensitizer. Waterhouse found that eosin (tetrabromofluorescein) could be used as a green sensitizer for collodion plates[17b,18] and was superior to coralline. Wet collodion plates sensitized with eosin and ethyl eosin were also used from about 1878 by A. and G. Braun for photographing paintings in the galleries of Madrid and St. Petersburg.

In 1882, Attout (called Tailfer) and Clayton found that eosin could be used to sensitize gelatin emulsions and obtained patents in England and France. Plates were made under these patents by several early manufacturers and termed *isochromatic* plates. Vogel used eosin as a sensitizer in the form of its silver salt. Plates so sensitized were manufactured by J. B. Obernetter of Munich and sold as "Obernetter-Vogel-Eosin-Silver Plates."

By 1883, Eder had systematically investigated the dyes of the eosin series as sensitizers and found that erythrosine (5) (tetraiodofluorescein) was especially valuable as a green sensitizer for gelatin emulsions and superior to eosin. Eder's results were published, and the first erythrosine-sensitized plates were made in 1884 by the firm of Löwy and Plener in Vienna and named *orthochromatic* plates. The use of erythrosine has continued to the present day.

Eder investigated the relation between the absorption and sensitizing bands of dyes more closely than had been done by Vogel and found that, in general, a dye sensitizes about 20–40 mμ farther towards the red than it absorbs.

In 1884 also, Vogel found that quinoline red, then newly discovered, could be used as a green sensitizer and retains its action if used together with cyanine, which is a red sensitizer. Vogel marketed a mixture of the dyes under the name of azalin,[19] with which plates were made. The new plates had poor keeping qualities and were still predominantly blue-sensitive, but by the use of strong yellow filters they could be used for photographing paintings. They were used by Kaiser and Runge in their researches on arc spectra.

Dyes of practically all the then known classes were examined as sensitizers, more than 140 being examined by Eder and Valenta alone.[20] Many were found which were effective to a slight extent but today are only of historical interest. Thus, those considered relatively outstanding among the azo dyes included fast red, congo red, glycine red, and benzo nitrol brown; in the rosaniline series, ethyl violet and formyl violet S4B; and among other dyes acridine orange, alizarine blue, discovered to be a sensitizer by Eberhard, the oxazines, indulines, and nigrosines. A serious defect of many of the dyes used in these early investigations was their desensitizing action, so that, although they conferred sensitivity to the longer wave length regions of the spectrum, sensitivity to white light was materially reduced.

The next step forward is due to Miethe and Traube,[21] who, in 1901, synthesized dyes especially for use as sensitizers. They prepared homologs of cyanine and later obtained bluish-red dyes by substituting quinaldine for lepidine. These were thought to be new dyes, but it was soon realized that they had been made before by Hoogewerff and VanDorp [22] and also by Spalteholz [23] and had been named isocyanines by the former.* A series of these isocyanines was prepared, the N,N-dimethyl and diethyl homologs proving the most satisfactory; the latter was named ethyl red (86). High purity was found essential for the best results, and their use produced much stronger sensitization in the green and yellow regions of the spectrum, although not in the red, than had previously been attained.

From then on, attention was concentrated on the cyanines, this group yielding much better sensitizers than any other. Aside from their photographic value, the cyanines have very little commercial significance; in general, they are far too fugitive for use as textile dyes.

The next developments are largely associated with the name of Dr. E. König, who worked in the laboratories at Hoechst (Farbwerke vorm. Meister, Lucius and Brüning). Miethe and Traube had been unable to extend the sensitizing range of their isocyanines toward the red by increasing the complexity of the alkyl groups attached to nitrogen; but König achieved the desired result by introducing substituents into the quinoline nuclei, thus weighting the dye molecule.[24] The substituted isocyanines so obtained were excellent sensitizers, both for collodion and gelatin emulsions, and were superior to anything previously available. Pinaverdol had one methyl group as a substituent and orthochrome (87) had two, and these were good green and yellow sensitizers. In pinachrome (88), two ethoxy groups were introduced, and it absorbed and sensitized farther into the red, while pinachrome violet (89), having two added dimethylamino groups, sensitized to still longer wave lengths.* The new dyes were protected by patents which were issued from about 1903 onward, and somewhat similar dyes and dye mixtures were marketed by other German manufacturers.

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* For the structure of the cyanine dyes and for their general chemistry, see Chapter XXIV. The numbers which follow the names of dyes refer to the formula numbers in that chapter.

None of these dyes was satisfactory as a red sensitizer, but in 1905 Homolka,[25] one of König's colleagues, found that a very good red sensitizer could be prepared by carrying out the ethyl red condensation in the presence of formaldehyde or chloroform. The new product was named pinacyanol (24) and recognized as belonging to a new and distinct group, although its structure remained obscure until Mills and Hamer, in 1920, showed that it belonged to the class which they termed carbocyanines, the nuclei being linked by the chain =CH—CH=CH— as compared with the =CH— linkage of the older cyanines.[26] In the meantime, however, it came into general use. Plates sensitized with pinacyanol combined with pinachrome were produced commercially as *panchromatic* plates by the firm of Wratten and Wainwright, Ltd., in 1906, and were much faster than the azalin-sensitized plates of an earlier era, so that the taking of instantaneous photographs by red light became practicable.

A dye similar in structure to pinacyanol but containing two β-naphthoquinoline nuclei was later prepared at Hoechst and called pinacyanol blue. The structure was not disclosed at the time, and the dye was rediscovered by Gutekunst [27] under the name of naphthocyanol.

In 1903, a patent [28] described the preparation of dyes by the action of alkali on 2- and/or 4-methylquinoline quaternary salts in the presence of an oxidizing agent. From a quaternary salt of 2,4-dimethylquinoline, a dye was obtained which sensitized for the red and infrared, and this was placed on the market under the name of dicyanine by the Hoechst Dye Works; and the same firm subsequently introduced a modification, dicyanine

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* For the absorption spectra of these dyes, see Figure 382, p. 1023.

A, which contained ethoxy groups as substituents. The structure of these dyes was not known until 1924, when Mills and Odams [29] showed that the dicyanines belong to the carbocyanine group and are, in fact, 2,4′-carbocyanines (25). The sensitizing action of the dicyanines was not intense, and they were unstable and difficult to apply satisfactorily; nevertheless, their action extended far into the infrared, and, using them, Merrill,[30] Meggers,[31] and Brackett [32] photographed lines in the solar spectrum to about 985 mμ, thereby approaching although not surpassing, the point reached by Abney.[6]

In 1919, Adams and Haller, working at the U. S. Department of Agriculture, Bureau of Chemistry, discovered a new dye of unknown structure which they accordingly named kryptocyanine.[33] The dye was produced by the action of alkali on lepidine ethiodide in the presence of formaldehyde and was later shown by Mills and Braunholtz to be a 4,4′-carbocyanine [34] (26), the nuclei being linked by the chain =CH—CH=CH—, as in the case of pinacyanol and dicyanine. This dye was an excellent infrared sensitizer, having an intense band between 700 and 800 mμ, the maximum being at about 750 mμ. Kryptocyanine sensitizes quite differently from dicyanine. It is stable and easy to use and can be added to the emulsion with excellent results, so that ready-sensitized materials could be made without difficulty. This dye presented many possibilities. The photography of the spectrum as far as 800 mμ became easy, but beyond this point the dye had very little power and at 900 mμ was inferior to dicyanine.

In 1925, while preparing kryptocyanine, H. T. Clarke of the Kodak Research Laboratories noticed that the dye was accompanied by a second, less soluble one. This dye, which was named neocyanine (95), was tested as a sensitizer by Dundon, Schoen, and Briggs [35] and found to sensitize from 650 mμ to 900 mμ for moderate exposures, the maximum being at 820 mμ. Hypersensitizing of the sensitized plate with ammonia made easy the photography of the spectrum to well beyond 1000 mμ and Babcock, of the Mount Wilson Observatory, recorded lines as far as 1163 mμ.[36]

The demand for sensitizing dyes for use in aerial photography had caused their manufacture to be started in 1916 in England

and the United States. In England, investigations were carried on at the Cambridge University Laboratories under Pope and Mills[37] and culminated in a series of papers by the latter and his collaborators, from 1920 to 1928, in which the structures of all the cyanines then known were established. Although Mills' research in the cyanine dye field ceased at this point, it provided an effective stimulus in various directions to which others were not slow to respond. By showing that pinacyanol, dicyanine, and kryptocyanine are dyes in which the nuclei are linked by the bridge =CH—CH=CH— as compared with the corresponding linkage =CH— in the simple cyanines, Mills pointed the way to the further lengthening of the connecting chain; and developments in this direction have, indeed, provided most striking advances in photographic sensitizing.

Progress continued in several directions. Pinaflavol was discovered in 1920 by Schuloff, who condensed *p*-dimethylaminobenzaldehyde with *α*-picoline ethiodide. This dye is a powerful green sensitizer and belongs to a class related to the true cyanines, although distinct from them. Although other members of the class are strong sensitizers, they show, in general, a tendency to fog the emulsion.

The isocyanines of E. König and the dyes such as pinacyanol, dicyanine, and kryptocyanine are derivatives of quinoline; but it was found that valuable sensitizers could also be obtained by employing nuclei derived from bases such as benzoxazole, benzothiazole, benzoselenazole, and thiazoline. Cyanines containing the benzothiazole ring had, indeed, been made in 1887 by Hofmann[38] but attracted little attention until Mills reopened the problem in 1922.[39] After the elucidation of the structure of carbocyanines by Mills and Hamer,[26] a much-improved method for their preparation was devised by W. König * and applied to a number of different nuclei by him[40] and by Dr. Hamer at the Ilford laboratories.[41] The latter also described improved preparations of *pseudocyanines*, in which class a 2-quinoline nucleus is linked to a second nucleus which can be the same or dissimilar.[42]

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* Professor at the Technical High School at Dresden and no relative of Dr. E. König at Hoechst.

Several of the newer dyes were much more powerful than the older dyes; thus, 3,3′-diethylthiacarbocyanine iodide (90), called thiazole purple * by König, is a much better green and yellow sensitizer and gives less fog than, for example, orthochrome. By employing naphthothiazole nuclei in place of the benzothiazole nuclei of this dye, Hamer and Brooker independently obtained red sensitizers superior to pinacyanol.[43] A further advance was made by Hamer, who prepared thiacarbocyanines containing the chain =CH—CMe=CH— in place of the unsubstituted chain of earlier dyes;[44,43a] and some of these dyes as well as others with different substituents at the center of the three-carbon chain[45] have proved of great practical value. The use of these dyes led to the preparation, in 1929, of *supersensitive panchromatic* emulsions which reached new high levels of speed. A contribution of value was made by Piggott and Rodd, Imperial Chemical Industries, Ltd., who discovered a simple way of making unsymmetrical carbocyanines[46] and, thus, further increased the number of available sensitizers.

Enhanced sensitivity was achieved in certain other ways. In 1920, Bloch and Renwick[47] of the Ilford Laboratories published an account of experiments in which they had increased the sensitivity throughout the spectrum of optically sensitized layers by the addition of *auramine*, a yellow dye which alone is almost if not entirely inert as a sensitizer. Later, Mees discovered that combinations of certain sensitizing dyes gave greatly enhanced sensitivity instead of the depressed sensitivity that it had long been held was the general result of using dye mixtures; his results were made the subjects of patents.[48]

From about 1930 onward, very active synthetic work was pursued in the industrial laboratories; and many patents were granted to the Ilford, Agfa, and Kodak Companies. The large number of sensitizers available enabled these firms to market films and plates having a wide range of sensitizing for commercial and scientific purposes.

The number of sensitizers has been considerably augmented in recent years by the discovery of a large new group known as the *merocyanines*. These are characterized by the amide grouping

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* The dye is almost magenta in solution, but *purpur* in German signifies a much redder shade than the purple of modern English.

$>N-(\overset{|}{C}=\overset{|}{C})_n-\overset{|}{C}=O$, whereas the cyanines contain the amidinium ion system $>N-(\overset{|}{C}=\overset{|}{C})-\overset{|}{C}=\overset{+}{N}<$. The merocyanines, which were discovered independently by Kendall [49] and Brooker,[50] form the subject of a large number of patents. They are non-ionized dyes and are especially effective sensitizers for the shorter wave length portions of the visible spectrum.

Progress in infrared photography has been marked. Cyanines with the chain $=CH-CH=CH-CH=CH-$ (*dicarbocyanines*) were made according to a patent of W. König [51] and were efficient deep red and infrared sensitizers. In *tricarbocyanines*, the nuclei were linked by the chain $=CH-CH=CH-CH=CH-CH=CH-$; and these dyes, prepared in Germany and England independently by three sets of workers,[52] gave infra-red sensitizers much superior to neocyanine. Xenocyanine (64), the tricarbocyanine from lepidine, was prepared by Brooker.[53] Its maximum is at about 980 mμ, but the resonance lines of helium at 1083 mμ can be photographed without difficulty.

Using intermediates suggested by the work of W. König,[54] Brooker and Keyes synthesized cyanines containing the chains

$$-(CH=CH)_2-C(OAc)=(CH-CH)_2=$$

and

$$-(CH=CH)_2-C(OAc)=(CH-CH)_3=$$

and named them *tetra* and *pentacarbocyanines* (70), respectively.[55] The dyes are of value in spectroscopy and made possible the photography of "several hundreds of new lines beyond 1300 mμ in the spectra of the rare gases." [55a] Dieterle and Riester [56] have described the preparation of tetra- and pentacarbocyanines unsubstituted in the chain, and these are said to be more powerful than the dyes described above with acetoxy in the chain.

The progress effected in the photography of the spectrum by the application of dyes may be summed up in an approximate form in Figure 370. At the top are shown the visible spectrum and that portion of it which could be photographed on a collodion plate through glass apparatus before Vogel discovered the use of sensitizing dyes, which extended the photographic spec-

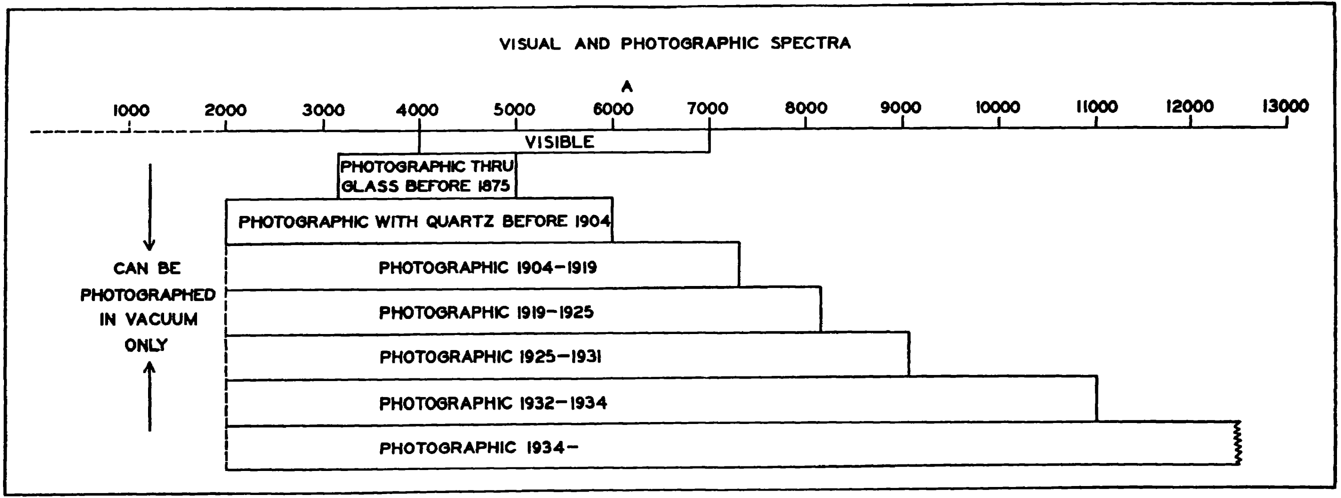


FIG. 370. Chart showing progress in the photography of the spectrum.

trum to 600 mμ. The discovery of pinacyanol in 1904 extended the photographic spectrum to beyond 700 mμ. The use of dicyanine is ignored here, though it was found by a few workers to extend the photographic spectrum to beyond 800 mμ. This wave length was easy to reach only after the discovery of kryptocyanine in 1919, while the production of neocyanine in 1925 extended the range to 900 mμ. Xenocyanine, made first in 1931, enabled 1100 mμ to be reached, and the pentacarbocyanines extended the photographic spectrum to beyond 1200 mμ.

The infrared limit of photographic reproduction can hardly be extended much farther. Thermal decomposition is bound to prevent the existence of stable dyes which absorb radiation with wave lengths longer than 2000 mμ, and the strong absorption which water shows around 1400 mμ will probably form a limit for the use of photographic emulsions.

There is no limit for photographic sensitivity at the shortwave end of the electromagnetic spectrum. The photographic plate registers the whole range of X-ray radiation as well as the γ rays beyond that region. The effect of X rays and γ rays on the photographic emulsion has not been discussed in this book, nor the photographic action of corpuscular rays.

In Figure 371 are wedge spectra (Chapter XVIII, p. 688) showing the effect of sensitizing chloride, bromide, and bromoiodide emulsions with erythrosine and with a thiacarbocyanine dye. In Figures 372, 373, 374, and 375, are shown wedge spectra obtained on plates made by sensitizing a slow chlorobromide emulsion of high contrast with a considerable number of sensitizing dyes. Where the structure is given in Chapter XXIV, the reference number is inserted. In Figure 372 (1–6) the dyes are chiefly cyanines; Figures 372 (7), 373, and 374 (1) are carbocyanines; Figure 374 (2), a dicarbocyanine; Figure 374 (3–7), a series of infrared cyanines; while Figure 375 shows the sensitizing effect of some miscellaneous dyes, including two merocyanines, 375 (4) and 375 (5).

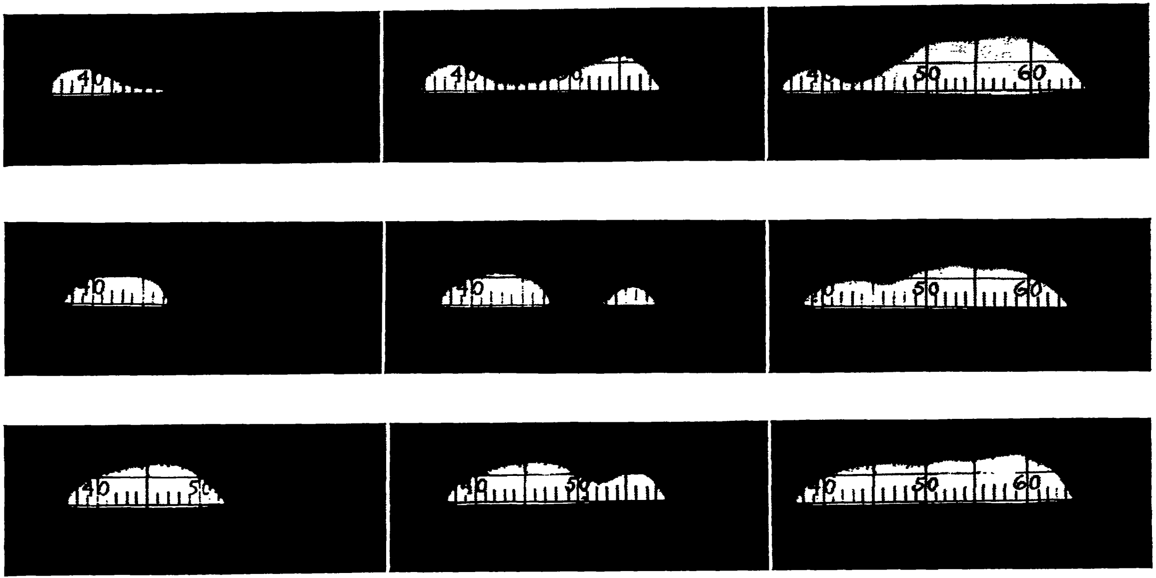
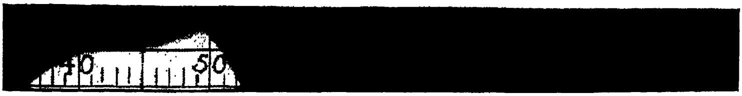
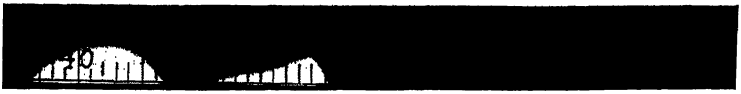


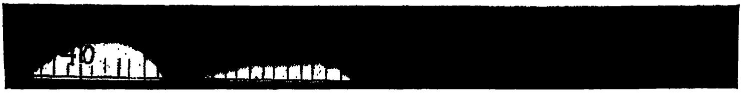
FIG. 371. Wedge spectrograms of chloride, bromide, and bromo-iodide emulsions sensitized with erythrosine and a thiacarbocyanine.



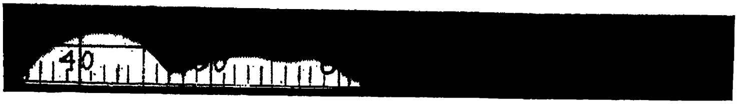
1. 3,3′-diethyl-4,5,4′,5′-dibenzothiacyanine chloride.



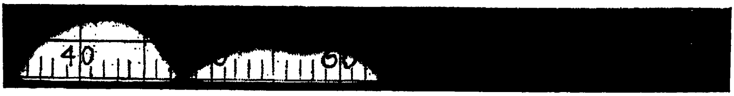
2. 1,1′-diethyl-2,2′-cyanine iodide.



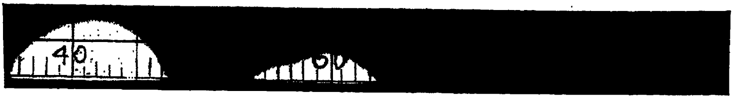
3. 1,1′-diethyl-2,4′-cyanine iodide (ethyl red) (86).



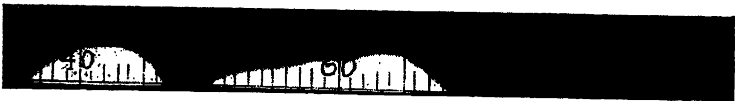
4. 1,1′-diethyl-6,6′-dimethyl-2,4′-cyanine bromide (orthochrome T) (87).



5. 1,1′-diethyl-6,6′-diethoxy-2,4′-cyanine bromide (pinachrome) (88).

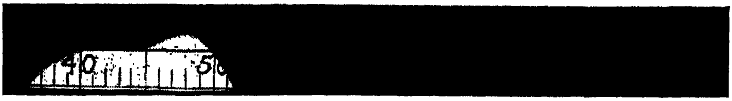


6. 1,1′-diethyl-4,4′-cyanine iodide (cyanine blue).

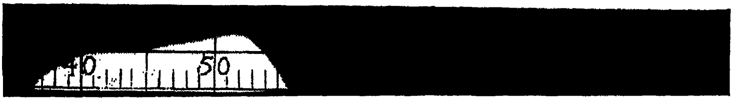


7. 1,1′-diethyl-2,2′-carbocyanine iodide (pinacyanol) (24).

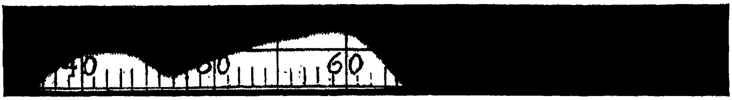
FIG. 372. Wedge spectrograms of a chlorobromide emulsion sensitized with cyanine dyes.



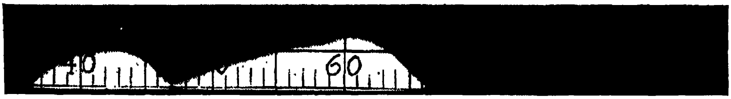
1. 3,3′-diethyl-thiazolino-carbocyanine iodide.



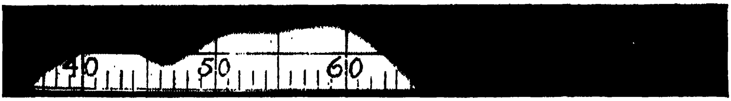
2. 3,3′-diethyl-oxacarbocyanine iodide.



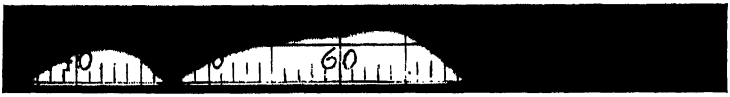
3. 3,3′-diethyl-thiacarbocyanine iodide (90).



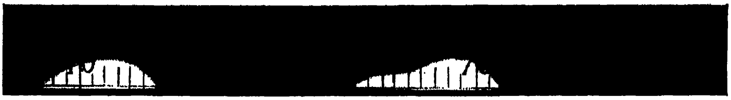
4. 3,3′-diethyl-selenacarbocyanine iodide.



5. 3,3′-diethyl-9-methyl-thiacarbocyanine iodide.

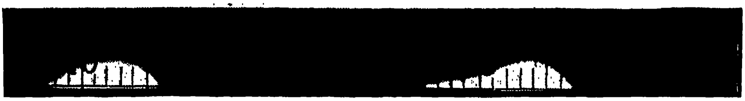


6. 3,3′-diethyl-4,5,4′,5′-dibenzothiacarbocyanine bromide (92).

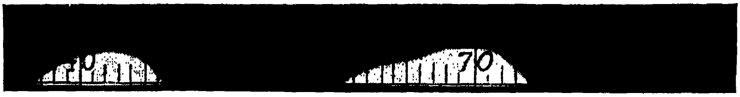


7. 1,1′-diethyl-2,4′-carbocyanine iodide (dicyanine) (25).

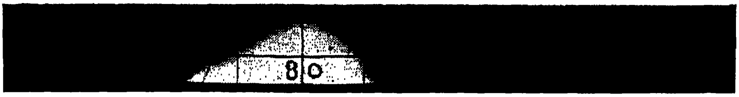
FIG. 373. Wedge spectrograms of a chlorobromide emulsion sensitized with carbocyanine dyes.



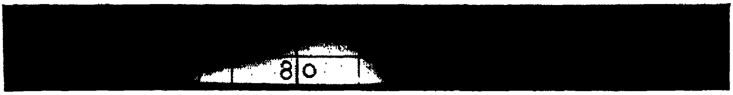
1. 1,1′-diethyl-4,4′-carbocyanine iodide (kryptocyanine) (26).



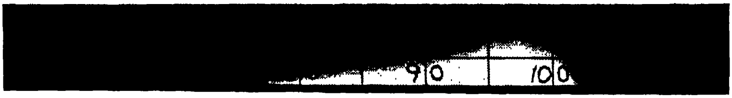
2. 3,3′-diethyl-thiadicarbocyanine iodide (52).



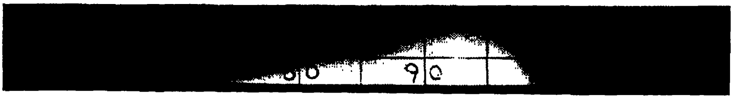
3. 3,3′-diethyl-thiatricarbocyanine iodide.



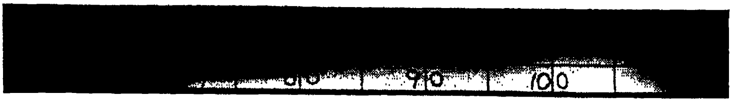
4. Neocyanine (95).



5. 1,1′-diethyl-4,4′-tricarbocyanine iodide (xenocyanine) (64).

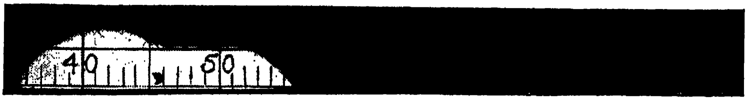


6. 12-acetoxy-3,3′-diethyl-thiatetracarbocyanine perchlorate (70).

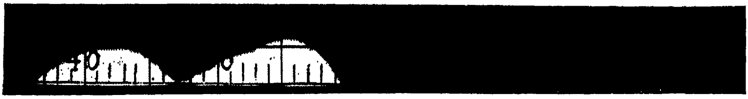


7. 12-acetoxy-3,3′-diethyl-thiapentacarbocyanine perchlorate (70).

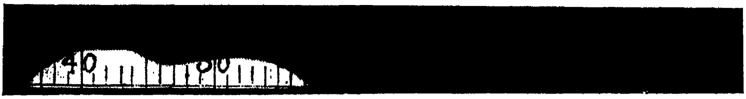
Fig. 374. Wedge spectrograms of a chlorobromide emulsion sensitized with infrared sensitizers.



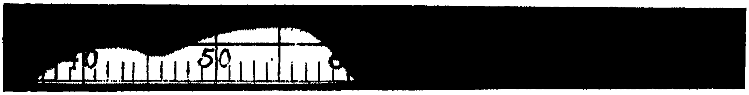
1. Acridine orange (10).



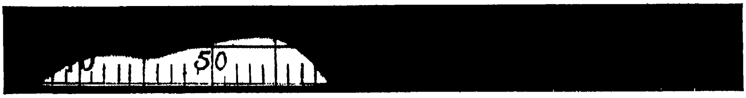
2. Erythrosine (5).



3. Pinaflavol (12).



4. 3-ethyl-5-[(3-ethyl-2(3)-benzoxazolylidene) ethylidene]-rhodanine.



5. 2-diphenylamino-5-[(3-ethyl-2(3)-benzothiazolylidene ethylidene]-4(5)-thiazolone.

FIG. 375. Wedge spectrograms of a chlorobromide emulsion sensitized with some miscellaneous dyes.

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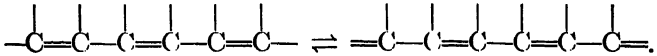
CHAPTER XXIV

THE SENSITIZING AND DESENSITIZING DYES

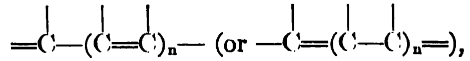
ORIGIN OF COLOR IN ORGANIC COMPOUNDS

According to modern views, the color of organic compounds is usually associated with the presence in the molecule of a long chain of atoms, predominantly carbon, linked by alternate single and double bonds and forming a so-called *conjugated chain.* For intense colors, the sequence of linkages in such a chain should be readily reversible according to the scheme:



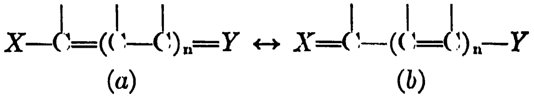
$$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}- \rightleftharpoons =\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=.$$

If the chain consists of an uneven number of carbon atoms, the general formula may be written



$$=\overset{|}{C}-(\overset{|}{C}=\overset{|}{C})_n- \quad (\text{or } -\overset{|}{C}=(\overset{|}{C}-\overset{|}{C})_n=),$$

where *n* is zero or a positive integer. If the chain is terminated with the hypothetical atoms *X* and *Y*, as in formula (1), a transition from (*a*) to (*b*) may occur if the valency of *X* is raised from one, in (*a*), to two, in (*b*), and if the valency of *Y* is simultaneously lowered from two, in (*a*), to one, in (*b*). Transition from (*b*) to (*a*) may be brought about by these valency changes taking place in the reverse direction.



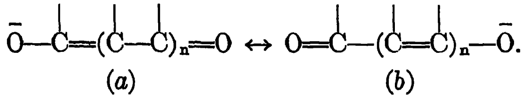
$$\underset{(a)}{X-\overset{|}{C}=(\overset{|}{C}-\overset{|}{C})_n=Y} \leftrightarrow \underset{(b)}{X=\overset{|}{C}-(\overset{|}{C}=\overset{|}{C})_n-Y} \qquad (1)$$

Actually, a system such as this provides the essential color-conferring group for the vast majority of dyes. The conjugated chain stretching between the terminal atoms *X* and *Y* corresponds to the *chromophore* of Witt's theory of color,[1] while the terminal atoms *X* and *Y* correspond to his *auxochromes.**

***These terms are retained in modern usage but have been given more precise significance from the standpoint of the resonance theory.**

For the dye to be deeply colored, the forms (1*a*) and (1*b*) must be of comparable stability, and the raising or lowering of the covalency of X and Y must take place with ease. Actually, very few atoms are capable of fulfilling these requirements for X and Y and, of the few, the most important are oxygen and nitrogen.

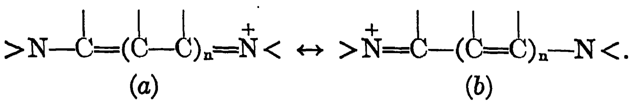
If both X and Y are oxygen atoms, system (1) may be given the general representation



$$\underset{(a)}{\overset{-}{\mathrm{O}}-\overset{|}{\mathrm{C}}=(\overset{|}{\mathrm{C}}-\overset{|}{\mathrm{C}})_n=\mathrm{O}} \leftrightarrow \underset{(b)}{\mathrm{O}=\overset{|}{\mathrm{C}}-(\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}})_n-\overset{-}{\mathrm{O}}}. \qquad (2)$$

This system carries a single negative charge and represents an anion in which the charge is shared between two oxygen atoms rather than carried by only one. It is seen that reversal of the sequence of the linkages is accompanied by the transfer of the negative charge from one end of the chain to the other.[2] A compound possessing a system such as (1) or (2) is not considered to be in a state of tautomeric equilibrium between the two extreme states (*a*) and (*b*) but as an actual hybrid between them and is, thus, called a *resonance-hybrid.*[3] This condition is implied by the double-headed arrow (↔) between the formulas representing the extreme resonance configurations. The latter have no real existence but must be regarded as intellectual or mathematical concepts which serve to define the compound.

If both X and Y are nitrogen atoms, the *auxo-chromophore*[*] becomes in its most general statement:



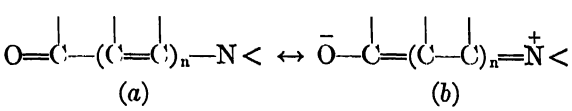
$$\underset{(a)}{>\mathrm{N}-\overset{|}{\mathrm{C}}=(\overset{|}{\mathrm{C}}-\overset{|}{\mathrm{C}})_n=\overset{+}{\mathrm{N}}<} \leftrightarrow \underset{(b)}{>\overset{+}{\mathrm{N}}=\overset{|}{\mathrm{C}}-(\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}})_n-\mathrm{N}<}. \qquad (3)$$

Here, again, rhythmic shifting of the double and single linkages is accompanied by the transfer of a charge from one end of the chain to the other; but now a positive charge is involved, the nitrogen atoms being alternately tertiary (uncharged) and quaternary (charged). The system as a whole carries a single positive charge and, in fact, represents a complex cation in which a charge is shared between two nitrogen atoms rather than being associated with only one, as in the ammonium ion. In system (3), as in (2), the actual state of the compound is considered to be that of a resonance hybrid between the two extreme configurations (*a*) and (*b*).

---

[*] Witt's terminology does not include a single expression for the combination of the chromophoric chain and the terminal auxochromic atoms, and the term *auxo-chromophore* is used here to indicate this concept.

So far both X and Y have been considered as oxygen atoms or as nitrogen atoms, but one may be oxygen and the other nitrogen, as in scheme (4). A compound containing this system is regarded as a hybrid between the two hypothetical states



$$O{=}\overset{|}{C}{-}(\overset{|}{C}{=}\overset{|}{C})_n{-}N< \;\leftrightarrow\; \overset{-}{O}{-}\overset{|}{C}{=}(\overset{|}{C}{-}\overset{|}{C})_n{=}\overset{+}{N}< \qquad (4)$$

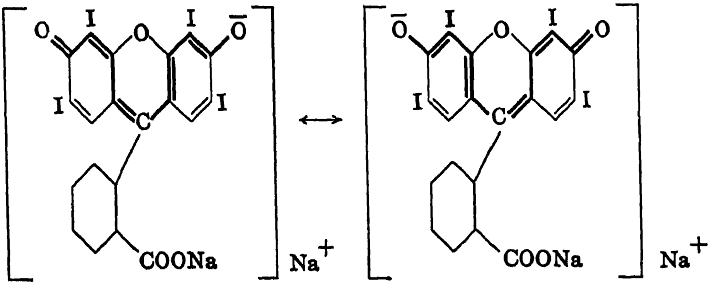
(*a*) (*b*)

(*a*) and (*b*), the first being uncharged and the second an electrical dipole. These extreme states are not identical and therefore differ in internal energy, but it may be deduced that the more closely (*a*) and (*b*) approach each other in internal energy, the more intense will the color become, the absorption coefficient increasing. This approach to equality in the extreme states is known as the *degeneracy* of the system.

If, in formula (2), n is made equal to 0, the formula becomes that of the carboxyl ion, and this system may accordingly be termed the *carboxyl-ion* type of auxo-chromophore. The simplest representative of formula (3) is, similarly, an *amidinium ion;* and (4) likewise represents the *amide* system. In all three systems, the essential and peculiar relation of the terminal atoms, the auxochromes, to the connecting chain, the chromophore, can be maintained only if the latter consists of an *uneven* number of carbon atoms; therefore, in proceeding from a chain of a given length to the next higher length of chain consistent with this relationship, *two* carbon atoms must be added, and these in the form of the group $-\overset{|}{C}{=}\overset{|}{C}-$ (or $=\overset{|}{C}{-}\overset{|}{C}=$). The group $-\overset{|}{C}{=}\overset{|}{C}-$ is known as *vinylene,* and, hence, series of compounds related to each other by containing chains of atoms having greater or fewer numbers of vinylene groups are called *vinylene homologous* series; and the general formulas (2), (3), and (4), in fact, represent such series, since with increasing values of n the number of vinylene groups in the chromophoric chain is increased. In the following sections, the importance of these various systems in actual dyes will be discussed, but certain other systems are known and are mentioned later.

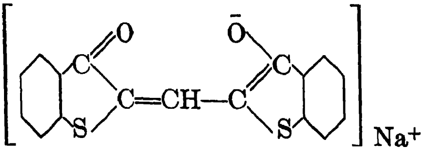
DYES CONTAINING THE CARBOXYL-ION SYSTEM; THE PHTHALEINS

The phthalein dyes probably constitute the most important group conforming to the carboxyl-ion system and include several important photographic sensitizers. Thus, *erythrosine* may be represented as



(5)

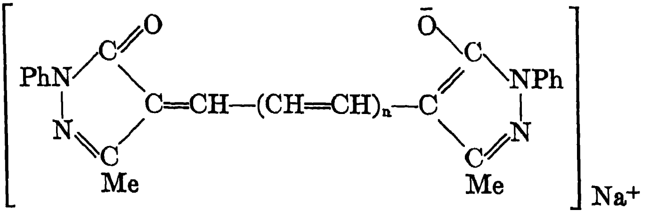
The conjugated chain essential for resonance (the *chromophore*) is indicated by heavy lines. In 1932, Schneider[4] described dyes



(6)

of the structure shown in formula (6) as being sensitizers for the green portion of the spectrum.

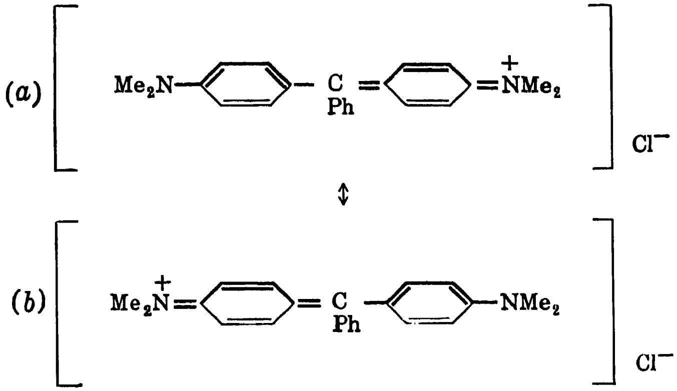
Certain dyes of formula (7) ($n = 0, 1, 2$) have been patented by Gaspar[5] for use as antihalation dyes.



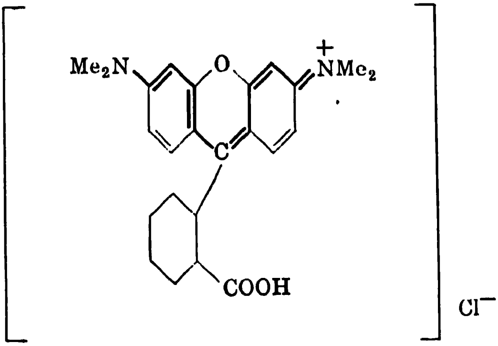
(7)

DYES CONTAINING THE AMIDINIUM-ION SYSTEM

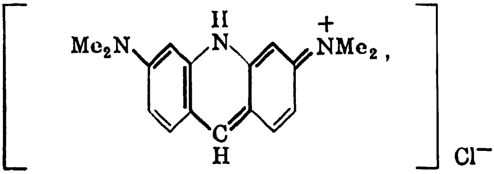
A number of important dye classes contain the amidinium-ion system. The following examples give formulas for the triphenylmethane dye *malachite green* (8), the pyronine dye *rhodamine* (9), the acridine dye *acridine orange* (10), the cyanine dye *pinacyanol* (11), and the styryl dye *pinaflavol* (12). In each formula, the conjugated chain linking the two nitrogen atoms of the



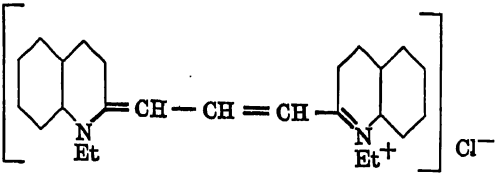
(8)



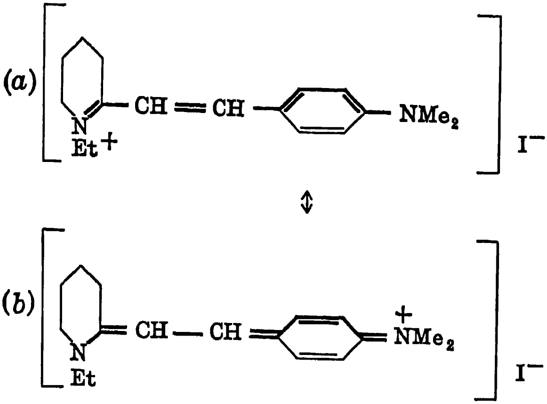
(9)



(10)



(11)



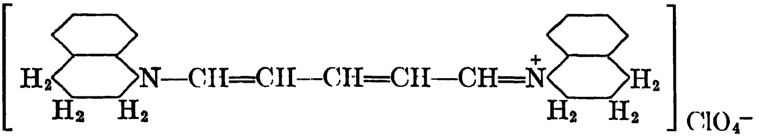
(12)

amidinium-ion system is emphasized by thickened lines. These dyes are seen to be complex ammonium salts in which the color-conferring system is in the cation; and it is possible to draw two resonance formulas in each case, although to save space this is done in only two instances: The first case chosen is malachite green (8), in which the molecule is symmetrical about the central carbon atom; and, consequently, the two extreme resonance configurations, (8*a*) and (8*b*), are identical except for their disposition in space. Dyes (9), (10), and (11) are symmetrical, likewise, and give rise to two identical extreme resonance configurations. The second instance is pinaflavol (12), in which the molecule is not symmetrical; and, consequently, the two extreme resonance configurations, (12*a*) and (12*b*), are not identical.

Of the various classes represented, the cyanines are outstandingly useful as photographic sensitizers and are described in detail.

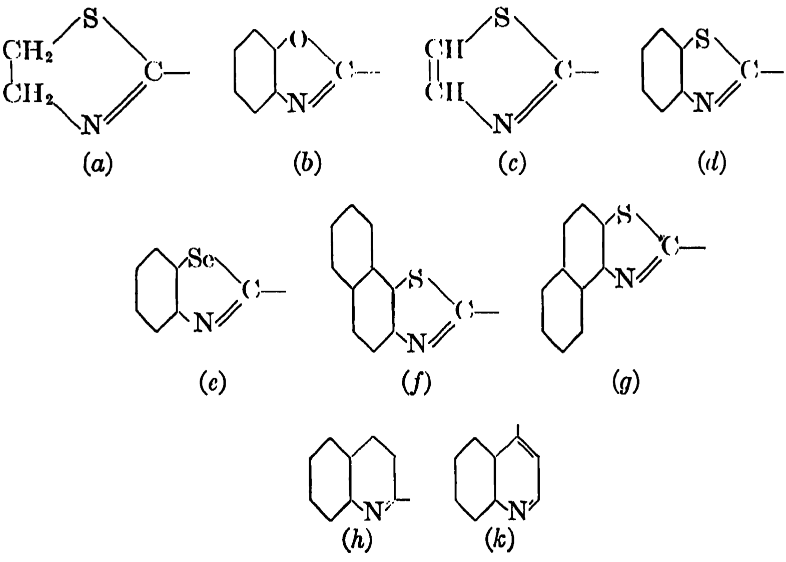
THE CYANINE DYES

The cyanines may be defined as dyes conforming to the amidinium-ion system (3) but in which both nitrogen atoms are members of heterocyclic ring systems and in which the conjugated chain joining these nitrogen atoms passes through a part of each heterocyclic ring. Of the five dyes formulated above, therefore, only (11) is a cyanine, since in (8), (9), and (10) neither of the nitrogen atoms is in a heterocyclic nucleus, and in (12) only one is. Further, in dye (13), glutaconaldehydeditetrahydroquinolide perchlorate, both nitrogen atoms are in heterocyclic rings, but the conjugated chain joining them does not pass through any part of the periphery of these rings; and (13) is, therefore, not considered a true cyanine. These distinctions are, of course, quite arbitrary but are useful in practice.


(13)

Heterocyclic Nuclei of Cyanine Dyes

Among the most important heterocyclic nuclei (14) employed in cyanine dyes are those of thiazoline (*a*), benzoxazole (*b*), thiazole (*c*), benzothiazole (*d*), benzoselenazole (*e*), α-naphthothiazole (*f*), β-naphthothiazole (*g*), 2-quinoline (*h*), and 4-quinoline (*k*). With these nuclei, linkage to the rest of the molecule

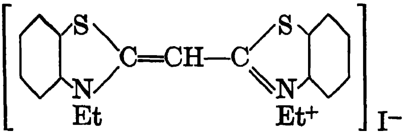

(*a*) (*b*) (*c*) (*d*)

(*e*) (*f*) (*g*)

(*h*) (*k*)

(14)

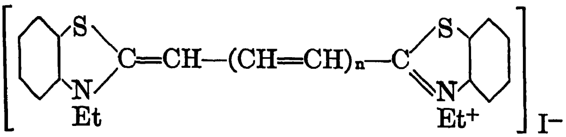
is effected through the α-carbon atom (to nitrogen) as indicated in (*a*)–(*h*); in (*k*), however, the linkage is through the γ-carbon atom. Groups, usually alkyl, such as methyl, ethyl, allyl, but also such as benzyl and *o*-nitrophenyl, are attached to the nitrogen atoms of these rings. As seen in formula (11), an acid radical is shared between the nitrogen atoms of the two nuclei. Structure (15) is an example of a simple cyanine derived from the benzothiazole nucleus with ethyl groups attached to the nitrogen atoms. In this dye, the nitrogen atoms are linked by a conjugated chain containing three carbon atoms.



(15)

The Cyanine Dye Chain

In the amidinium-ion system (3), the nitrogen atoms are linked by an *uneven* number of carbon atoms. To increase the length of the conjugated chain in formula (15), for instance, it must be raised from three to five carbon atoms. Repetition of the process leads to a seven-carbon chain, and in fact (16) is the general formula for this series of cyanine dyes, each of which contains two benzothiazole nuclei. The conjugated chain is lengthened by two carbon atoms, *i.e.*, by the vinylene group —CH=CH—, in proceeding from one member to the next. In such a vinylene homologous series, the first member has $n = 0$ and is a monomethine cyanine (*e.g.*, (15)), the group =CH— being known as methine or methenyl.



(16)

Dyes with the next higher length of chain, =CH—CH=CH—, trimethine cyanines, have been known for a long time; but their structure was first elucidated by Mills and Hamer,[6] who named dyes containing such a linkage *carbocyanines*. From this precedent, dyes containing the linkage =CH—$(CH{=}CH)_2$— are called *dicarbocyanines;*[7] those with $=CH-(CH=CH)_3-$, *tricarbocyanines,*[8] and so on.

The Relation of the Length of Chain to Absorption

Increasing the length of the chain in a cyanine dye results in the absorption being shifted markedly towards the longer wave lengths with each vinylene group added. This may be illustrated in the case of the series of dyes in formula (16), the absorption spectra being given by curves *A*, *B*, *C*, and *D* in Figure 376, where n = 0, 1, 2, and 3 for the cyanine, carbocyanine, dicarbocyanine, and tricarbocyanine, respectively. The shifts in wave length between successive maxima are considerable and approximate 100 mμ, as shown in the following table:[9]

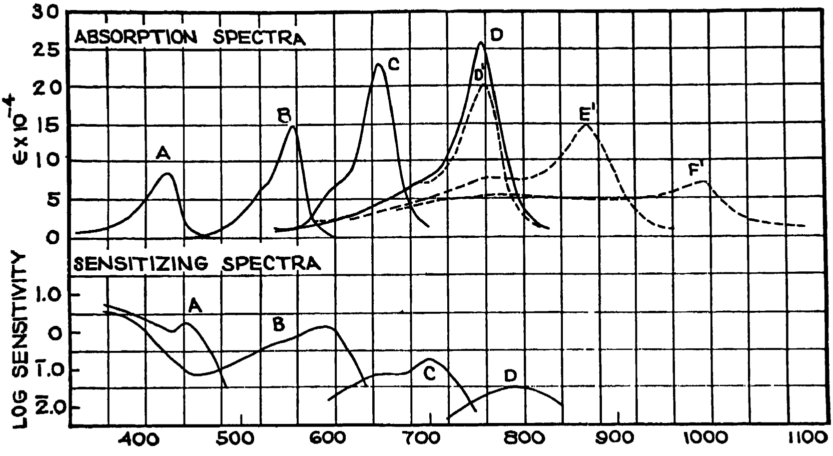


FIG. 376. Absorption spectra of dyes dissolved in methanol: *A*, *B*, *C*, *D*, dyes of the structure shown in formula (16) when n = 0, 1, 2, 3, respectively; *D'*, *E'*, *F'*, dyes of formula (17) when n = 1, 2, 3, respectively. Sensitization curves for dyed silver chloride emulsion: *A*, *B*, *C*, *D* correspond to the sensitivities conferred by dyes of formula (16) when n = 0, 1, 2, 3, respectively.

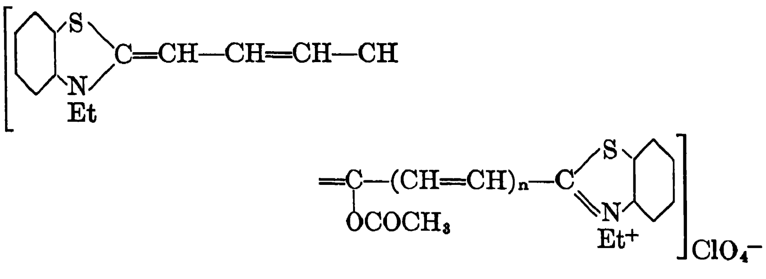
TABLE LXXXV

WAVE LENGTHS OF MAXIMUM ABSORPTION OF THE CYANINES OF FORMULA (16)

n	$\lambda_{max.}$ *in mμ*	*Difference in mμ*
0	423	
		134
1	557	
		93
2	650	
		108
3	758	

Similar results have been obtained for cyanines derived from nuclei other than benzothiazole.[10] In general, lengthening the chain linking the nuclei in a cyanine dye by the addition of vinylene shifts the absorption, on an average, about 100 mμ toward the longer wave lengths. Thus, an alcoholic solution of the monomethine cyanine (16) ($n = 0$), which absorbs in the ultraviolet and blue parts of the spectrum, is yellow; and the color becomes red if the chain is increased in length from $=\mathrm{CH}-$ to $=\mathrm{CH}-\mathrm{CH}=\mathrm{CH}-$ (16), ($n = 1$), the absorption for this compound being in the green part of the spectrum. The addition of another vinylene group (16), ($n = 2$) shifts the absorption to the red part of the spectrum, the color of the solution being blue; and the last member of the series (16), ($n = 3$) absorbs in the infrared region and gives a solution which is greenish blue.

The absorptions of this series of four dyes span more than the whole of the visible spectrum; that of the dye having the longest chain, in fact, lies well in the infrared region. It follows that, if the addition of further vinylene groups produced shifts similar to those already observed, dyes could be obtained which would absorb still farther in the infrared. These chains cannot be lengthened indefinitely, however, since limitations are imposed both by the methods of synthesis (p. 1005) and by the stability of the compounds, which, in general, diminishes as the length of the chain increases. The tricarbocyanine (16), ($n = 3$) is readily prepared and is comparatively stable, but the next higher vinylene homologue ($n = 4$), the tetracarbocyanine, is much less stable; and the pentacarbocyanine[11] ($n = 5$) is still less so. However, long-chain carbocyanines of the formula (17) ($n = 1$, 2, and 3) carrying the acetoxy group as a substituent in the chain are somewhat more readily prepared, and their behavior



(17)

as sensitizers is described by Brooker and Keyes.[12] The absorptions of these three vinylene homologues are also shown in Figure 376 (D', E', F'). The two highest homologues are very unstable in dilute alcoholic solutions, and the values of ϵ, the molecular extinction coefficient, are correspondingly uncertain although the values of λ_{max} are believed to be correct. The curve of the lowest member of the series ($n = 1$), the 10-acetoxy-tricarbocyanine, has a value of λ_{max} almost identical with that of the unsubstituted dye (16), ($n = 3$), so that the effect of the acetoxy group on λ_{max} is negligible. If this is assumed to hold for the higher vinylene homologues also, the dyes of the six different chain lengths may be regarded to this extent as a single vinylene homologous series. The λ_{max} values are plotted in Figure 377 as functions of the number of double bonds in the conjugated chain, and it is seen that the points indicate a linear relationship such as was found by Lewis and Calvin[13] for cyanine series up to and including the tricarbocyanines.

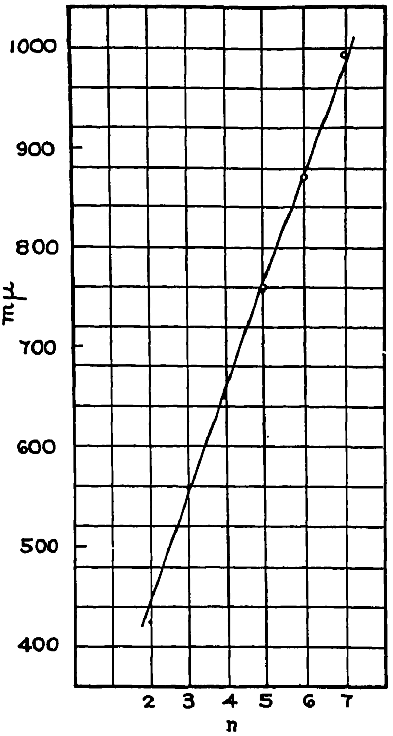


FIG. 377. Values of λ_{max} for the absorption of dyes (•) of formula (16) when $n = 0, 1, 2, 3$; and (o) of formula (17) when $n = 1, 2, 3$, plotted against the number of double bonds in the conjugated chain joining the nitrogen atoms.

In Figure 376 is shown also a comparison between the absorption curves of the vinylene homologous series (16) ($n = 0, 1, 2$, and 3) and the sensitizations that these dyes confer on silver halide. For this comparison, the dyes were incorporated in a silver chloride emulsion, optimum quantities of each being employed, and the sensitizing curves determined on an equal energy basis. The maxima of sensitivity in this series invariably lie at somewhat longer wave lengths than the absorption maxima; but, aside from this, the similarity between the two sets of spectra is remarkable.

Color Values of the Various Heterocyclic Nuclei

The first member of the series ((16), $n = 0$) gives a pale yellow solution and is, thus, relatively light-colored; if the two sulfur atoms in this dye are replaced by oxygen atoms, giving two benzoxazole nuclei, the absorption is shifted almost entirely into the ultraviolet region, and the "dye" is practically colorless in solution. The higher vinylene homologues of this benzoxazole compound also are lighter in color * than the corresponding benzothiazole dyes. The various heterocyclic nuclei (14) have different color values, the order in which they are given in (14) being that of increasing depth of color when symmetrical cyanines are considered. Thus, a cyanine containing two thiazoline nuclei (a) is lighter than one of the same chain length containing two benzoxazole nuclei (b), and the nucleus that gives the greatest depth of color is the 4-quinoline nucleus (k). This relationship is brought out in Figure 378, in which the wave lengths of

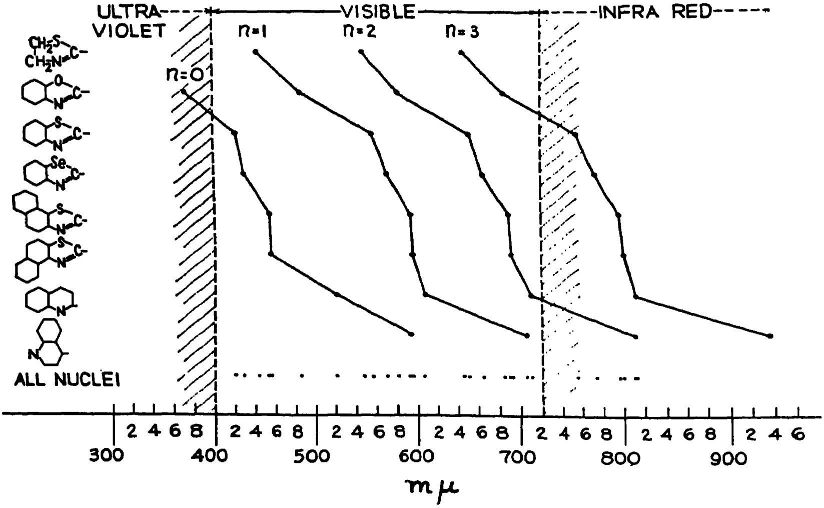


FIG. 378. Wave lengths of maximum absorption in methanol solution of eight vinylene-homologous series of cyanines.

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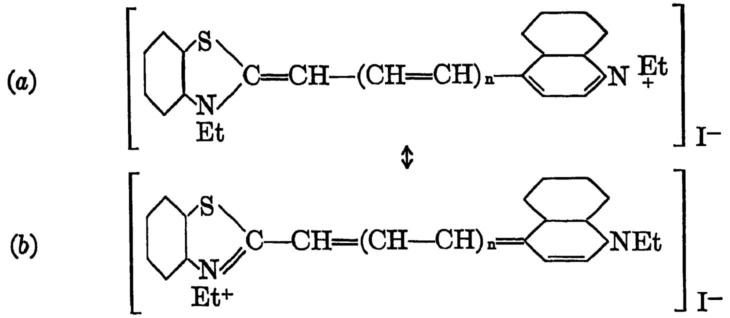
* As used in this chapter, this term means that the absorption band lies nearer the violet.

maximum absorption of eight series of symmetrical cyanines are shown, these being similar in structure to (16) (n = 0, 1, 2, 3) but with the various nuclei indicated replacing the benzothiazole rings of (16) in seven of the series. In all cases the maxima are those of cyanines in which ethyl groups are attached to the nitrogen atoms, these being used exclusively for the sake of uniformity. The individual segments of the four curves for n = 0, 1, 2, 3 are reasonably parallel to each other with but one exception, showing that the various nuclei retain their relative color values irrespective of the length of chain in the dyes compared. The exception is that the segment for n = 0 between the β-naphthothiazole and 2-quinoline nuclei is not parallel to the corresponding segments for higher values of n. This is because the vinylene shifts between the first and second members of the vinylene homologous series are greater if the nuclei are benzoxazole, benzothiazole, benzoselenazole or α- or β-naphthothiazole than if they are 2- or 4-quinoline.

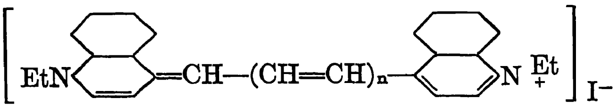
The maxima are also projected as dots in a line at the bottom of the figure to show the wide variety of absorptions (and, hence, of sensitizings) given by these eight series of dyes.

Unsymmetrical Cyanines

Only those cyanines have been considered hitherto which contain two identical nuclei, but methods are available for preparing unsymmetrical cyanines in which the heterocyclic nuclei are dissimilar. It is clear that the wide assortment of possible nuclei and chain lengths makes the number of possible unsymmetrical combinations very large indeed, and a great number have been prepared. The absorption characteristics of many have been analyzed by Hamer and her colleagues,[14] from which it may be concluded that, in general, unsymmetrical cyanines absorb either at, or reasonably near, the mean of the absorptions of the parent symmetrical dyes. This is illustrated in Figure 379, in which are plotted the absorption maxima (λ_{max}) of a typical series of three unsymmetrical cyanines (18), (n = 0, 1, 2), each containing a benzothiazole nucleus and a 4-quinoline nucleus, together with the absorption maxima of the related symmetrical dyes (16), (n = 0, 1, 2) and (19), (n = 0, 1, 2). In each of the three sets of comparisons, the observed value of λ_{max} for the unsymmetrical dye is seen to be very close indeed to the arithmetic mean of the wave lengths of the related parent dyes, in spite of



(18)



(19)

the fact that the parent dyes differ widely in absorption.

It has been shown that the relationship described above does not hold if the two nuclei in the unsymmetrical dye are of widely

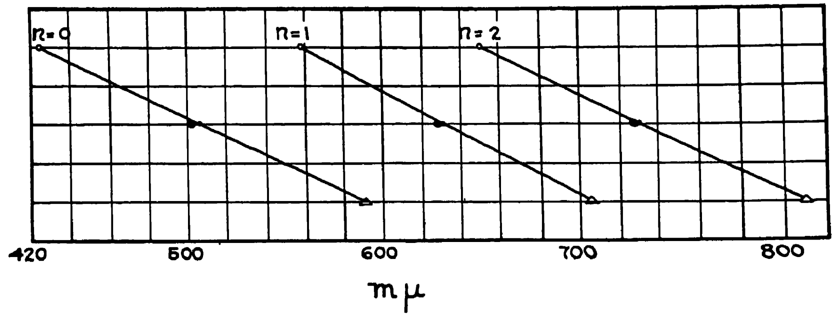
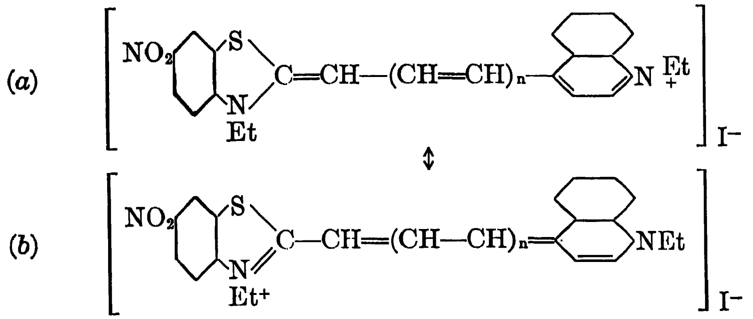


FIG. 379. Values of λ_{max} in methanol of a series of three unsymmetrical cyanines of the structure shown in formula (18) when $n = 0, 1, 2$ (●); those of the parent symmetrical dyes of the structure shown in formula (16) when $n = 0, 1, 2$ (○); and in formula (19) when $n = 0, 1, 2$ (△).

different basicity.[9] If one is strongly basic and the other very feebly basic, the unsymmetrical dye will absorb at shorter wave length than that calculated from the maxima of the symmetrical dyes. Furthermore, the discrepancy between the observed and calculated values increases as the length of the chain increases. This is illustrated by the unsymmetrical series (20) ($n = 0, 1, 2$), the absorption maxima for which are given in Figure 380 with those of the related parent dyes. It is seen that the unsymmetrical dyes absorb at appreciably shorter wave lengths than those calculated, the discrepancy, indicated by the dotted lines, increasing as the chain joining the nuclei is lengthened. It follows that for such unsymmetrical dyes as (20) the relation between λ_{max} and the number of double bonds is no longer linear.



(20)

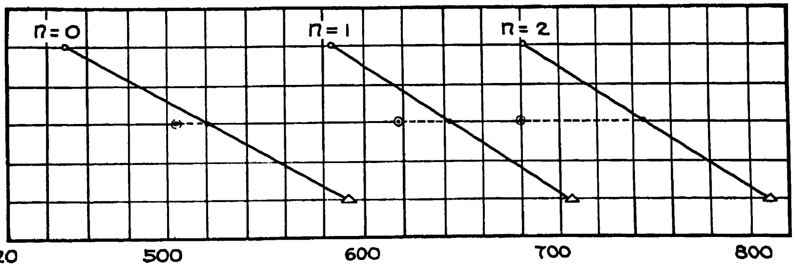
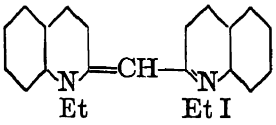


FIG. 380. Values of λ_{max} in methanol of a series of unsymmetrical cyanine dyes of the structure shown in formula (20) when $n = 0, 1, 2$ (⊙) and those of the parent symmetrical dyes in formula (16) but containing nitro groups in the 6 and 6′ positions, when $n = 0, 1, 2$ (○) and in formula (18) when $n = 0, 1, 2$ (△). The solid dot (⊙) indicates the arithmetic mean.

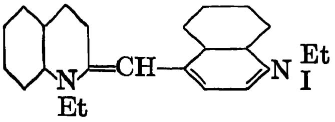
Influence of the Position of Attachment of Quinoline Nuclei in Cyanine Dyes

It has been pointed out on page 998 that the 2-quinoline nucleus (14, *h*) gives rise to cyanines of lighter color than those containing the 4-quinoline nucleus (14, *k*). The absorption spectra (in methanol) of the symmetrical monomethine cyanines containing these nuclei (and with ethyl groups attached to the nitrogen atoms), (21) and (23), are given in Figure 381. It is



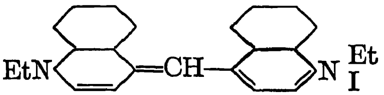
(21)

1,1′-diethyl-2,2′-cyanine iodide



(22)

1,1′-diethyl-2,4′-cyanine iodide



(23)

1,1′-diethyl-4,4′-cyanine iodide

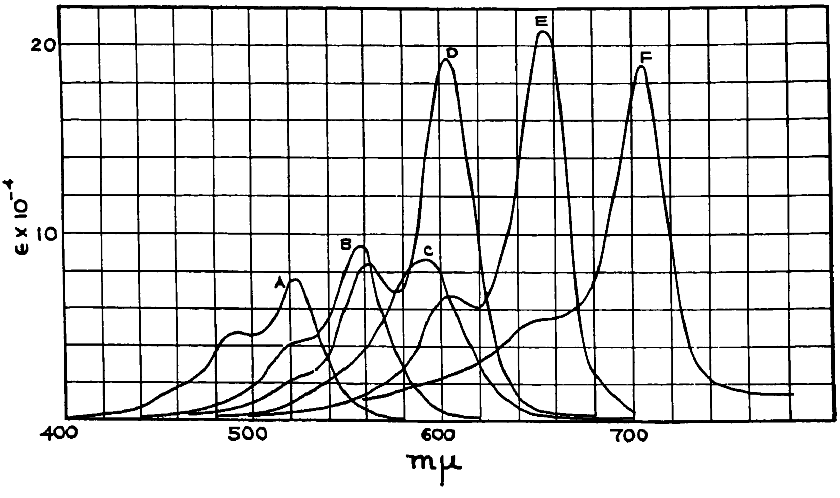
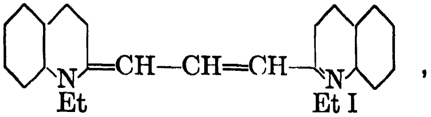


FIG. 381. Absorption spectra in methanol: *A*, formula (21); *B*, (22); *C*, (23); *D*, (24); *E*, (25); and *F*, (26).

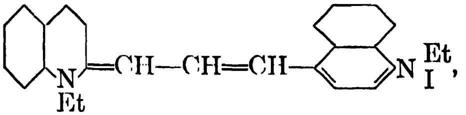
seen that dye (23) (curve *C*) absorbs with a maximum at longer wave length than dye (21) (curve *A*). This difference may be correlated with the fact that the dye with the nuclei linked through the 4 position (23) contains a longer conjugated chain than dye (21). Thus, the chain joining the nitrogen atoms in dye (23) comprises seven carbon atoms and contains four double bonds, whereas that in dye (21) comprises only three carbon atoms with two double bonds.

If a 2-quinoline nucleus is linked to a 4-quinoline nucleus (22), the absorption (Figure 381, *B*) falls almost exactly midway between the absorptions of dyes (21) and (23), and this may be correlated with the fact that in dye (22) the conjugated chain between the nitrogen atoms is of intermediate length between those in dyes (21) and (23) and comprises five carbon atoms with three double bonds. An arrangement identical with that of dyes (21), (22), and (23) exists in their next higher vinylene homologues, (24), (25), and (26), the absorption spectra of which are also shown in Figure 381 (curves *D*, *E*, and *F*). It is of interest to notice the much higher values of the molecular extinction coefficient, ϵ, for these trimethine cyanines compared with the monomethine cyanines (curves *A*, *B*, *C*). This increase in ϵ_{max} in a vinylene homologous series with increasing length of chain is a general phenomenon,[15] although one not without exceptions.



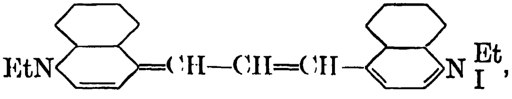
(24)

1,1′-diethyl-2,2′-carbocyanine iodide



(25)

1,1′-diethyl-2,4′-carbocyanine iodide



(26)

1,1′-diethyl-4,4′-carbocyanine iodide

Nomenclature of the Cyanines

The terms *cyanine, carbocyanine, dicarbocyanine*, etc., have already been defined. The method used to indicate the nuclei present in a cyanine was developed as follows:

The earliest known cyanines were monomethine dyes in which both nuclei were derived from quinoline. Since no other nuclei were involved, it was not necessary specifically to indicate the presence of quinoline, but only the point of attachment of the quinoline ring, it having been early realized that this could be linked through either the 2- or the 4-position (cf. preceding section). This was done indirectly by designating that type in which both quinoline rings were linked through the 4-position (23) as a *cyanine*, this being the first type discovered.*[16] Later, dyes in which a 2-quinoline nucleus was linked to a 4-quinoline nucleus (22) were discovered,[17] and these were distinguished as *isocyanines*. The remaining type with two 2-quinoline nuclei (21) was prepared much later[18] and was first called *pseudoisocyanine* and then *pseudocyanine*.[19]

In modern usage, the omission of a special prefix to designate quinoline is retained, but numbering is used to designate the position of attachment of the nuclei: type (21) being termed a 2,2′-cyanine; (22), a 2,4′-cyanine; and (23), a 4,4′-cyanine.

If the chains are longer than the single methine bridge =CH—, the requisite additional prefix is introduced. Thus (24) is called a 2,2′-carbocyanine and (19) ($n = 2$), a 4,4′-dicarbocyanine. The alkyl groups are indicated by the numbering employed in the parent rings, so that the full name for (24) becomes *1,1′-diethyl-2,2′-carbocyanine iodide.*

The presence of nuclei other than quinoline is indicated by a suitable prefix. The benzothiazole nucleus is indicated by *thia* and, thus, (15) is named 3,3′-diethylthiacyanine iodide, and the unsymmetrical dye (18) ($n = 1$) is named 1′,3-diethylthia-4′-carbocyanine iodide. In this name, as in general, the nucleus designated second is primed.

The benzoxazole nucleus is indicated by *oxa;* benzoselenazole, by *selena;* thiazole, by *thiazolo;* thiazoline, by *thiazolino,* and so on; but this method of naming has certain disadvantages, and an alternative system is used in Beilstein's *Handbuch,* according to which, for example, (24) becomes *bis[1-ethyl-quinoline-(2)] trimethincyanine iodide* and (18) ($n = 2$) becomes *[3-ethyl-benzothiazole-(2)]-[1-ethyl-quinoline-(4)] pentamethincyanine iodide.*

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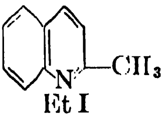
* The discovery of the first cyanine by Williams in 1856 places the class among the very oldest synthetic dyes, the first of these having been prepared by Perkin in the same year. The beautiful blue color of Williams' dye suggested the name *cyanine* (Gk. *kyanos* = dark blue), which, in turn, has provided a name for the whole group of related dyes although they may now be of practically any color.

Methods of Synthesis of Symmetrical and Unsymmetrical Cyanines.

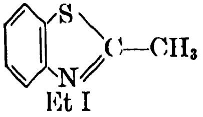
General. The reactions leading to the formation of cyanines are of the condensation type, *i.e.*, two (or more) molecules of reactants are brought together under suitable conditions, and dye is formed with simultaneous elimination of simple molecules, such as those of mineral acid, mercaptan, alcohol, water, aniline, or acetanilide. The components taking part in these reactions may be divided into two categories: The first component (*A*) contains reactive hydrogen, which furnishes the (ionizable) hydrogen of the mineral acid, mercaptan, alcohol, and so forth, listed above. The second component (*B*) contains a reactive negative atom or grouping such as halogen, cyano, alkyl- or arylmercapto, alkoxy, anilino, or acetanilido which combines with the reactive hydrogen of component *A*.

For a cyanine dye to be formed from a condensation reaction, either component *A* or component *B* or both must contain the necessary heterocyclic rings. Heterocyclic components of type *A* are essentially quaternary salts of heterocyclic bases containing methyl groups, such as quinaldine ethiodide (27), 2-methylbenzothiazole ethiodide (28), and lepidine ethiodide (29). In these compounds, the methyl groups occupy the α- or γ-position with respect to the nitrogen atom and are very reactive, losing hydrogen readily in condensation reactions. The reactivity of the methyl groups in these salts is doubtless related to their ability to yield external methylene bases, such as (30), (31), and (32):[20]



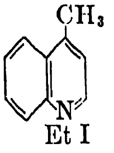
quinaldine
ethiodide

(27)



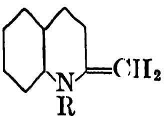
2-methylbenzothiazole
ethiodide

(28)

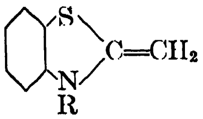


lepidine
ethiodide

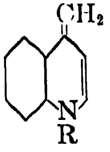
(29)



(30)

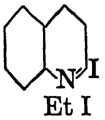


(31)



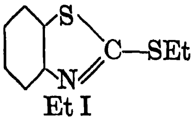
(32)

Heterocyclic components of type *B* are usually quaternary salts (sometimes bases) having a negative atom or grouping linked to the α- or γ-carbon atom of the heterocyclic nucleus, either directly or through a vinylene or polyvinylene chain. As examples of intermediates of this kind may be cited 2-iodoquinoline ethiodide (33) and 2-ethylmercaptobenzothiazole ethiodide (34), in which the negative groups are linked directly to the heterocyclic nucleus, and (35), in which the group is linked to the nucleus through a vinylene group:



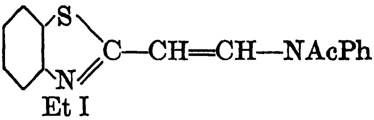
2-iodoquinoline ethiodide

(33)



2-ethylmercaptobenzothiazole ethiodide

(34)



2-β-acetanilidovinylbenzothiazole ethiodide

(35)

Non-heterocyclic components of type *A* comprise malonic and glutaconic acids, cyclopentadiene, and indene. Non-heterocyclic components of type *B* comprise a wide variety of substances and include formaldehyde, the haloforms, orthoesters of carboxylic acids, β-alkoxyacroleinacetal, and dianilides (or their salts) of the type PhNH—(CH=CH)$_n$—CH=NPh, where $n = 0, 1, 2$.

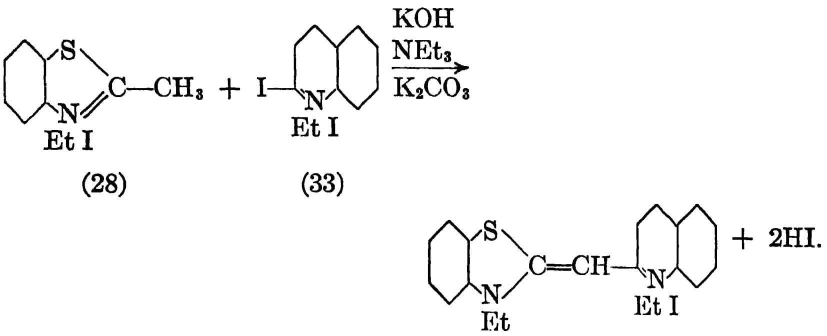
The methods of synthesis described here are classified according to the length of the methine or polymethine chain. Only the more important reactions can be dealt with, however, and for a more detailed account of synthetic procedures, the literature should be consulted. The reactions conform to three general types:

Type I, in which both components are heterocyclic;
Type II, in which only component *A* is heterocyclic;
Type III, in which only component *B* is heterocyclic.

Certain special types of cyanines are described in succeeding sections, and the methods by which they may be obtained are indicated in their respective sections.

Monomethine or "simple" cyanines. A very general reaction for preparing monomethine cyanines is that between a heterocyclic quaternary salt containing reactive methyl of type *A*, such as (27)–(29), and a heterocyclic component of type *B*, such as (33) or (34), this being a reaction of type I.

If the negative group is iodine, the reaction is:



(28) (33)

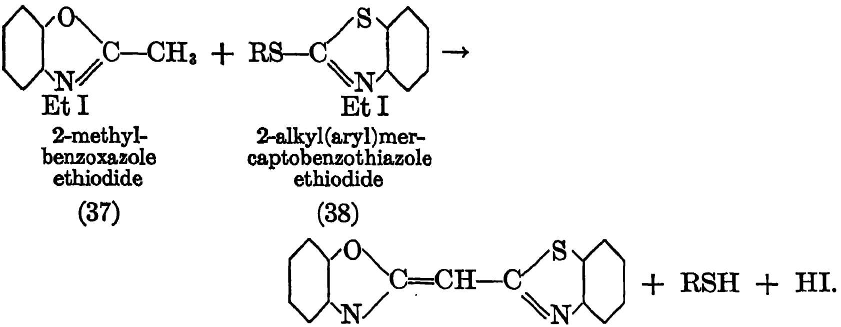
1,3-diethylthia-2′-cyanine iodide

(36)

Hydriodic acid is eliminated between the reactants, and condensation is therefore promoted by basic condensing agents. The benzothiazole salt (28) may be presumed to lose one molecule of HI, giving (31); and this then condenses with (33), with the loss of a second molecule of acid. Potassium hydroxide was employed at first for this type of reaction,[18,21] but triethylamine is superior,[22] as are the alkali carbonates.[23] In the example given, the product (36) is an unsymmetrical dye; but the reactive methyl group and iodine atom may be attached to nuclei of the same kind and so produce a symmetrical dye. This reaction has not failed with any quaternary salts containing reactive methyl to which it has been applied,[21b,22,24] but the heterocyclic derivatives containing reactive iodine are more restricted in number.

The place of the reactive iodine atom in the 2- position of quinoline may be taken by one in the 4- position, in which case dyes containing a 4-quinoline nucleus result.[25]

A second reaction of wide applicability consists in condensing a quaternary salt containing reactive methyl with an intermediate containing an alkyl- or arylmercapto group in a reactive position. The elements of acid and of mercaptan are eliminated, the former combining with the base used as condensing agent:



2-methyl-benzoxazole ethiodide

(37)

2-alkyl(aryl)mercaptobenzothiazole ethiodide

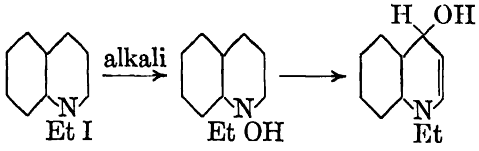
(38)

3,3′-diethyloxathiacyanine iodide

(39)

This method appears to be limited only by the availability[26] of the necessary mercapto-intermediates, although a wide variety of these have been used.

A method of limited applicability but of considerable historical interest consists of the condensation under the influence of alkali of a quaternary salt containing reactive methyl with a quinolinium salt having a free 4- position, acid being eliminated as well as two atoms of hydrogen. The latter is probably taken up by the excess of quinolinium salt that it is advantageous to employ.[25,27] The reaction is of considerable value in the preparation of dyes in which at least one quinoline ring is linked in the 4- position, and the early syntheses of 4,4′-cyanines and 2,4′-cyanines were of this type. It seems probable that condensation takes place through the intermediate formation of a pseudo-base, such as (41), which may be regarded as a heterocyclic compound with a reactive group attached.



quinoline ethiodide

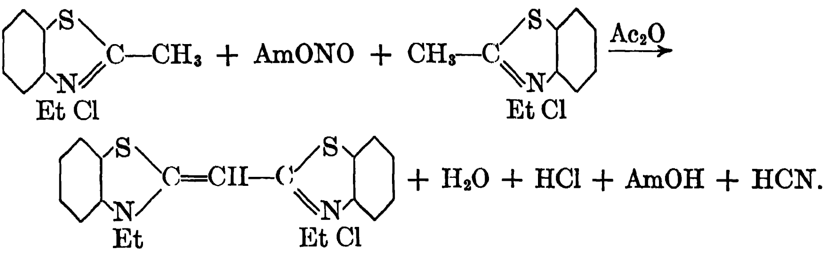
ammonium base

(40)

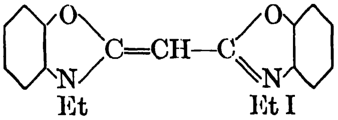
pseudo-base

(41)

In the monomethine cyanine series, there is but one known synthesis of type II. This consists in heating a quaternary salt containing reactive methyl with amyl nitrite in acetic anhydride solution. Amyl alcohol and the elements of mineral acid and of hydrocyanic acid are eliminated in this reaction, which appears to be of limited applicability and is best applied in the thiacyanine series:



This method was used by Fisher and Hamer in the preparation of *oxacyanines*,[28] such as (42), which is of especial interest in that

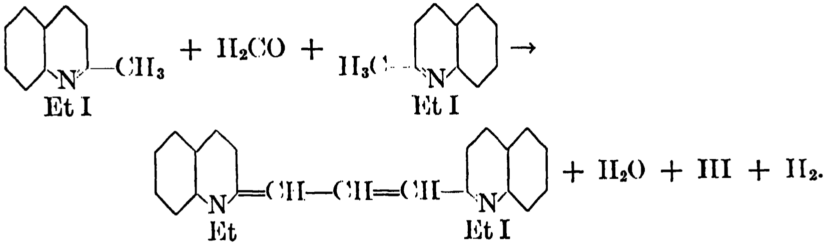


(42)

3,3′-diethyloxacyanine iodide

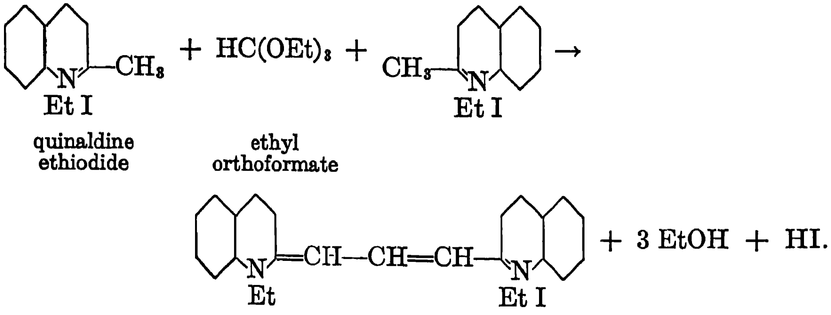
it absorbs so far in the ultraviolet (λ_{max} 370 mμ) that its solution is colorless; it was, in fact, the first colorless cyanine to be obtained.

Trimethine- or carbocyanines. Syntheses of symmetrical carbocyanines usually consist in the condensation of two molecules of a quaternary salt containing reactive methyl with a substance which provides the central =CH— of the three-carbon chain. Thus, Homolka obtained 2,2′-carbocyanine by treating with alkali a mixture of the ethiodides of quinaldine and quinoline to which formaldehyde had been added.[29] The quinoline ethiodide takes no active part in the reaction:



The formaldehyde may be replaced by a haloform;[30] and, in this case, only acid is eliminated from the reactants.

The most generally satisfactory method for the preparation of symmetrical carbocyanines is due to König[31] and consists in the condensation of a quaternary salt containing reactive methyl with ethyl orthoformate. In this reaction, alcohol and acid are eliminated, and the $-\overset{|}{C}H-$ group of the orthoester provides the central $=CH-$ group of the dye, thus:



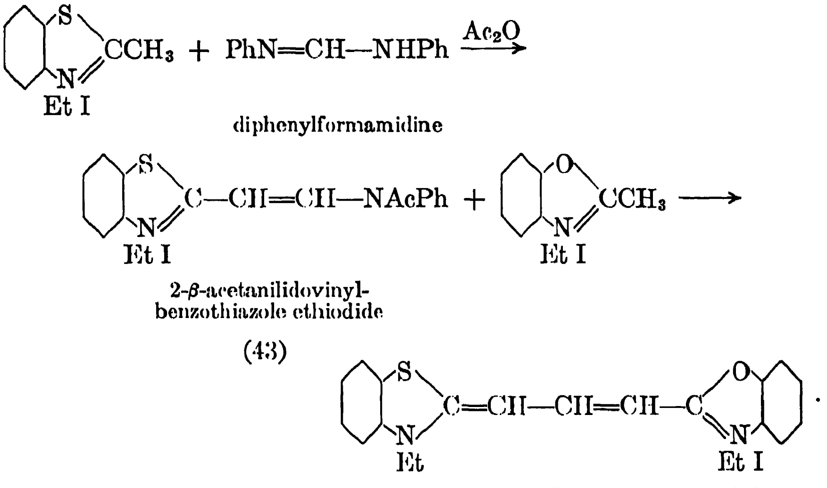
1,1′-diethyl-2,2′-carbocyanine iodide

König used acetic anhydride as a medium for the reaction; but Hamer[32] showed that greatly improved yields could be obtained by the use of pyridine, and her method has become standard for the preparation of dyes of this type. Symmetrical carbocyanines containing a wide variety of nuclei are thus obtainable.

Hamer further extended the method to the preparation of dyes with the chain $=CH-CMe=CH-$ by the use of ethyl orthoacetate in place of ethyl orthoformate, but this reaction cannot be applied to as many different types of quaternary salts as the orthoformate synthesis. The use of many other orthoesters of carboxylic acids in this type of reaction has been described by Brooker and White, so that a large number of symmetrical dyes have been prepared containing the chain $=CH-CG=CH-$, where G represents a variety of substituent groups.

A number of syntheses of type I are known in the carbocyanine series which are of especial value for the preparation of unsymmetrical dyes. The latter could theoretically be obtained by the condensation of a mixture of two different quaternary salts with formaldehyde, a haloform, or an orthoester; but the desired dye would be expected to be contaminated with the two related symmetrical dyes from which it could only be separated with considerable difficulty. However, this type of reaction has been applied successfully to the preparation of dyes of the 2,4′-carbocyanine (dicyanine) type[19] but has otherwise been little used.[33]

A general method for the preparation of unsymmetrical carbocyanines has been devised by Piggott and Rodd[34] and consists of the treatment of a quaternary salt containing reactive methyl with diphenylformamidine to give an intermediate capable of condensing with a second quaternary salt to give the desired dye. The first step in the synthesis may be brought about by fusing the components together or by heating them in acetic anhydride, in which case an acetylated intermediate such as (43) is formed.



diphenylformamidine

2-β-acetanilidovinylbenzothiazole ethiodide

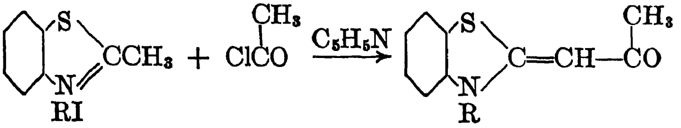
(43)

3,3′-diethyloxathiacarbocyanine iodide

(44)

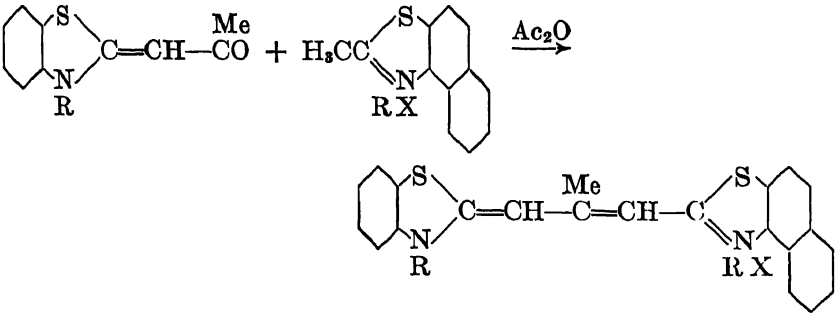
This reaction has enabled a large number of unsymmetrical carbocyanines to be prepared by workers in several laboratories. Working in media other than acetic anhydride, Ogata found that the acetylated intermediates gave much higher yields of product and were, therefore, more reactive than the unacetylated compounds.[35]

Chain-substituted unsymmetrical carbocyanines have been prepared by several methods. Brooker and White[36] have prepared reactive ketones, such as (45), by treating quaternary salts containing reactive methyl with acid chlorides in pyridine solution; and these ketones undergo condensation with a further proportion of quaternary salt in boiling acetic anhydride solution to give unsymmetrical dyes such as (46).[37]



2-acetylmethylene-3-alkyl-benzothiazoline

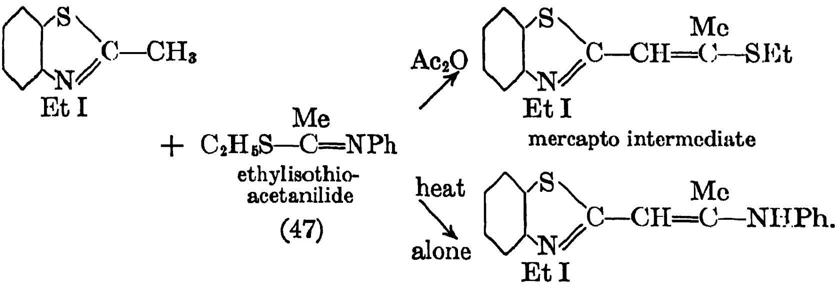
(45)



3,3′-dialkyl-9-methyl-4′,5′-benzothiacarbocyanine salt

(46)

A second method was patented by Koslowsky[38] and consists of the preparation of intermediates by the condensation of a quaternary salt containing reactive methyl with a substance of the type of ethylisothioacetanilide (47). The reaction is sup-



ethylisothio-acetanilide

(47)

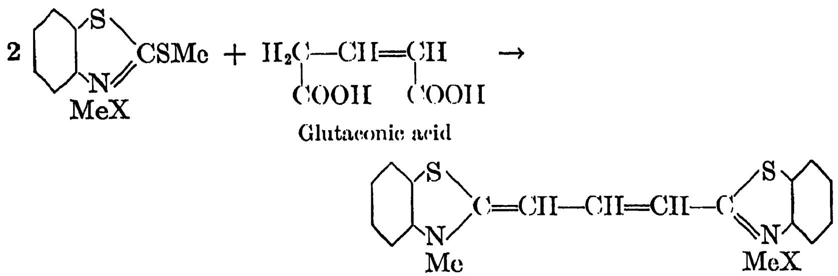
mercapto intermediate

anilino intermediate

(48)

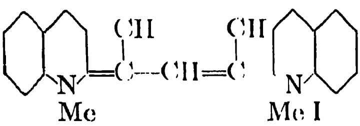
posed to take different courses, depending upon whether it is induced by heating the components alone or in the presence of acetic anhydride, the latter leading to a mercapto intermediate and the former to an anilino intermediate (48); but both types are stated to give chain-substituted carbocyanines on further treatment with a quaternary salt containing reactive methyl.

Several interesting reactions of type III are used in the carbocyanine series. One leading to unsubstituted carbocyanines was discovered by Kendall[39] and consists of the reaction of mercapto intermediates with glutaconic acid, the latter supplying the three-carbon chain of the dye. This method is of use where



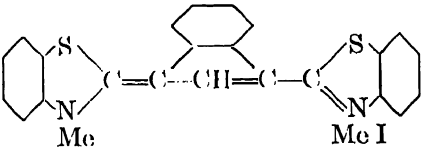
3,3′-dimethylthiacarbocyanine salt

mercapto intermediates are available but not the corresponding salts with reactive methyl. Similar reactions have been carried out by Kendall with compounds in which the —CH_2—CH=CH— chain forms part of a cyclic system, *e.g.*, *cyclo*-pentadiene and indene, the products being carbocyanines in which the three-carbon chain itself forms part of one of these cyclic nuclei, *e.g.*, (49) and (50).[40]



1,1′-dimethyl-9,10-vinylene-2,2′-carbocyanine iodide

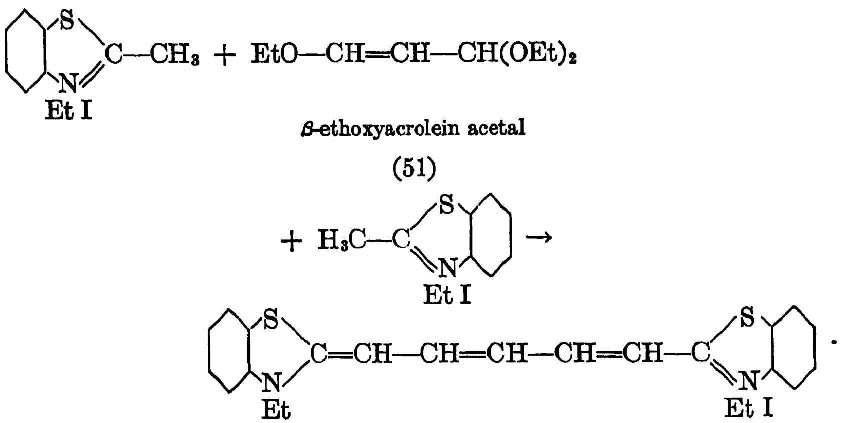
(49)



3,3′-dimethyl-8,10-*o*-phenylene-thiacarbocyanine iodide

(50)

Pentamethine- or dicarbocyanines. The first mention of the preparation of dicarbocyanines was made by W. König,[41] who indicated that they were obtainable by the treatment of quaternary salts containing reactive methyl with β-ethoxyacrolein acetal (51), the reaction being similar to that by which he obtained carbocyanines using ethyl orthoformate (p. 1010):



β-ethoxyacrolein acetal

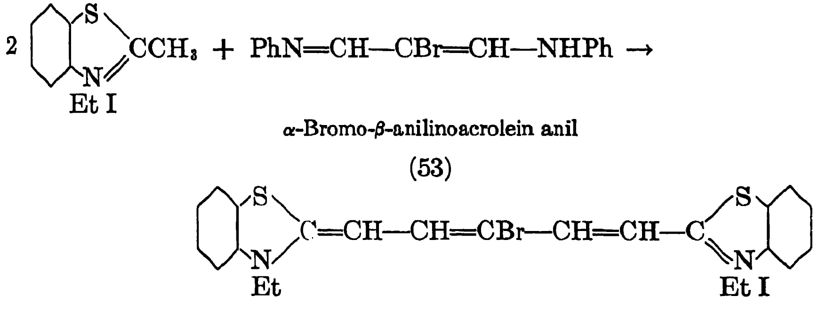
(51)

3,3′-diethylthiadicarbocyanine iodide

(52)

In spite of the practical and theoretical significance of the dyes involved, this brief reference was not followed by a more explicit account, although it is stated that many dicarbocyanines were made by this method.[42]

The first detailed account of dicarbocyanines was given by Beattie, Heilbron, and Irving,[7] who condensed heterocyclic salts containing reactive methyl with certain dianilides, *e.g.*, α-bromo-β-anilinoacrolein anil (53), the resulting dyes having the chain =CH—CH=C(halogen or nitro)—CH=CH— joining the nu-



α-Bromo-β-anilinoacrolein anil

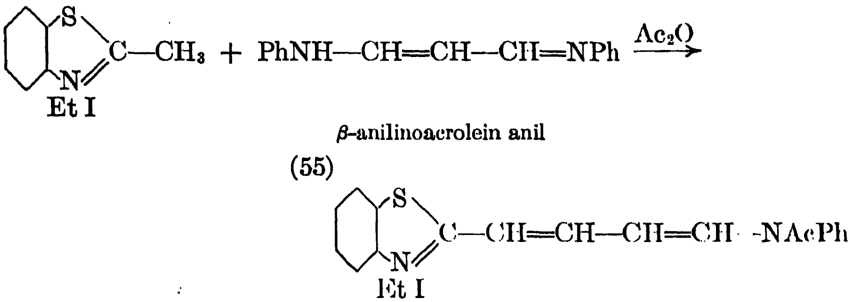
(53)

10-Bromo-3,3′-diethylthiadicarbocyanine iodide

(54)

clei. Heilbron and his colleagues worked on these chain-substituted dyes because the corresponding dianilides, such as (53), were more accessible than the unsubstituted compound (55), although that behaves similarly.[43,44]

By the condensation of equimolecular proportions of the unsubstituted dianilide (55) and a quaternary salt containing reactive methyl in acetic anhydride, Piggott and Rodd[45] obtained an intermediate, such as (56), capable of giving symmetrical or unsymmetrical dicarbocyanines on treatment with a second equivalent of quaternary salt, while similar intermediates (but unacetylated) are described by Zeh.[46]



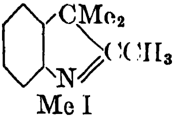
β-anilinoacrolein anil

(55)

2-(4-Acetanilidobutadienyl)benzothiazole ethiodide

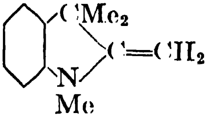
(56)

Heptamethine- or tricarbocyanines. In these dyes, the heterocyclic nuclei are linked by a chain of seven carbon atoms. They are described by three sets of workers. Wahl condensed the quaternary salt (57) (or the corresponding methylene base (58)) with a pyridinium compound, such as (59), or with a dye, such as (60), obtained by cleaving (59) with methylaniline, as indi-



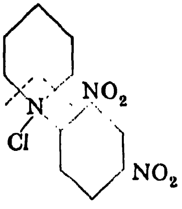
2,3,3-trimethyl-
indolenine
methiodide

(57)



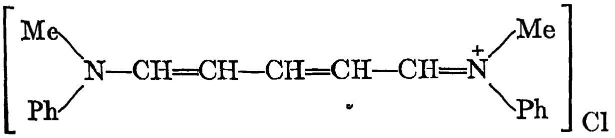
1,3,3-trimethyl-2-
methyleneindoline

(58)



2,4-dinitrophenyl-
pyridinium
chloride

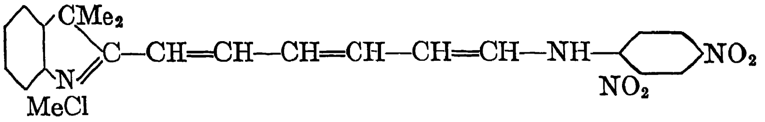
(59)



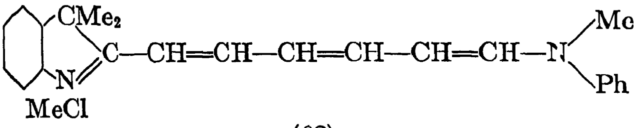
glutaconaldehyde dimethylanilide chloride

(60)

cated.[47] With equimolecular proportions of the reactants, an intermediate is formed of the type of (61) where (59) is used, the pyridine ring being broken in only one place, and (62) where (60) is used;[48,49] but with two proportions of salt to one of (59) or

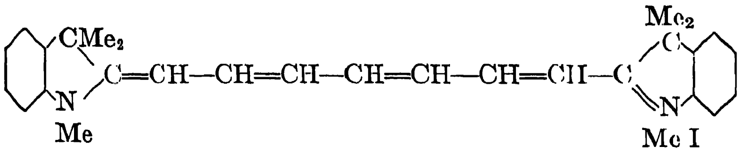


(61)



(62)

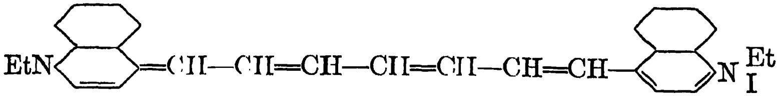
(60) the symmetrical tricarbocyanine (63) is formed, the five-carbon chain in (59) or in (60) forming the central portion of the tricarbocyanine chain.



1,3,3,1′,3′,3′-hexamethylindotricarbocyanine iodide

(63)

Piggott and Rodd also carried out a similar condensation with (60) to give (63),[45] while Fisher and Hamer[8] prepared a wide variety of tricarbocyanines from intermediates of the type of (59) or (60), preferably the latter, using alcoholic caustic alkali in most instances to effect the condensation. Brooker improved the yields of tricarbocyanines by using piperidine or triethylamine to effect the condensations[50] and succeeded in preparing 4,4′-tricarbocyanines, such as (64) (xenocyanine), which were not obtainable using alcoholic caustic alkali.

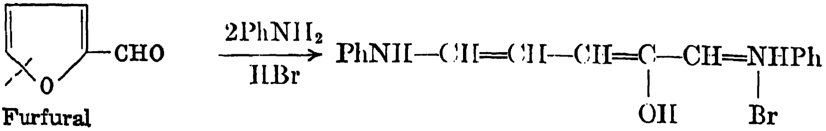


1,1′-diethyl-4,4′-tricarbocyanine iodide

(64)

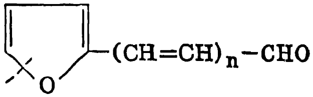
A number of unsymmetrical tricarbocyanines were prepared by Zeh using intermediates of the type of (62).[51]

Tetra- and pentacarbocyanines. Just as the pyridine ring of such compounds as (59) undergoes fission to give the open-chain compound (60), so the furane ring in furfural (65) is broken open, as indicated, by treatment with an aromatic amine and acid, giving a glutaconaldehyde dianilide salt with a hydroxyl group as substituent in the chain (66).[52] More important still, the reaction was applied by König to the higher vinylene homologues of (65), (67), (n = 1, 2) and, thus, di-tetrahydroquinolides of the type of (68) have been prepared, where n = 1 and 2.[53] These hydroxy dyes are unstable but are rendered stable by acylation, and the acylated derivatives (69) serve as intermedi-

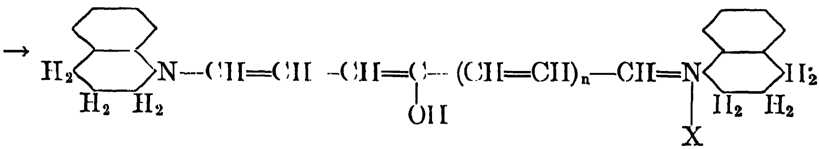


Furfural

(65) (66)

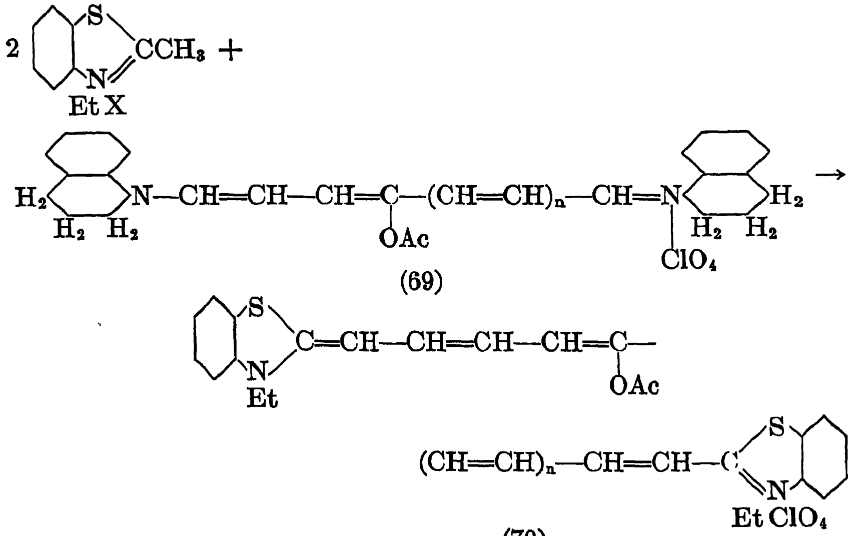


(67)



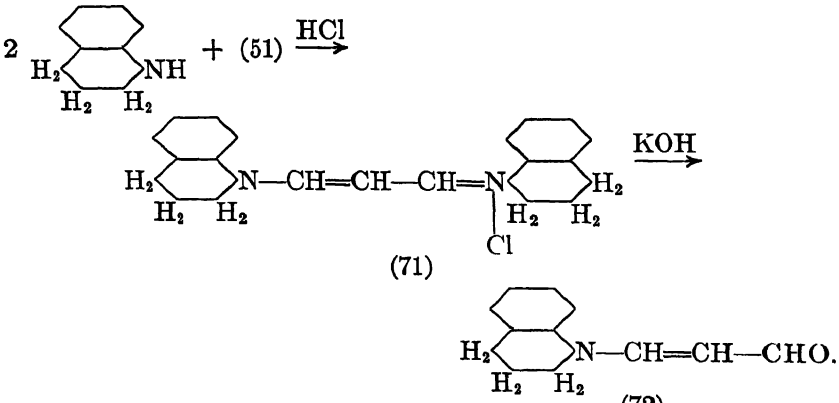
(68)

ates for the preparation of tetra- and pentacarbocyanines (70) (n = 1, 2) containing, *e.g.*, an acetoxy group as a substituent in the polymethine chain. Dyes of this type containing the chains shown in (70), where n = 0, 1, and 2, were patented by the I. G. Farbenindustrie A.-G.[54] Details of their sensitizing action are given by Brooker and Keyes [12] and by Dieterle and Zeh.[55]


(69)

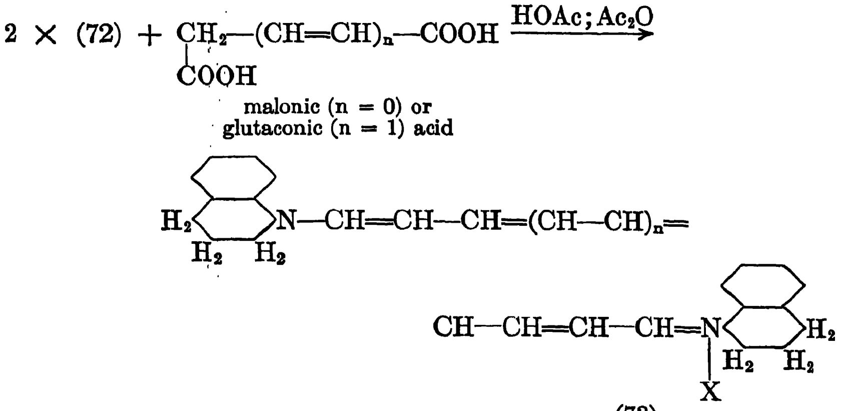
(70)

Dieterle and Riester have prepared tetra- and pentacarbocyanines unsubstituted in the chains. Tetrahydroquinoline is condensed with β-ethoxyacrolein acetal (51) under the influence of acid. The product (71) is hydrolyzed by caustic alkali to the


(71)

(72)

aldehyde (72), which is condensed with malonic acid or glutaconic acid to give a di-tetrahydroquinolide (73), (n = 0 or 1, respectively), which then serves as an intermediate for the desired tetra- or pentacarbocyanine.[11]

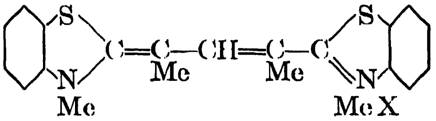


$$2 \times (72) + \underset{\displaystyle COOH}{CH_2}—(CH{=}CH)_n—COOH \xrightarrow{HOAc;\,Ac_2O}$$

(73)

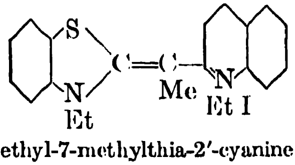
CYANINES DERIVED FROM QUATERNARY SALTS OF BASES CONTAINING REACTIVE SUBSTITUTED-METHYL GROUPS

The reactive methyl groups in the quaternary salts thus far described are unsubstituted; but König, Kleist, and Götze condensed 2-ethylbenzothiazole methiodide with ethyl orthoformate and obtained an 8,10-dimethylthiacarbocyanine (74).[56] 2-Ethyl- and propylbenzothiazole salts were also applied by Zeh and Schneider[57] to the preparation of symmetrical and unsymmetrical carbocyanines as well as of other types; and some of these dyes, such as the 7-methylthia-2′-cyanine (75), were patented



(74)

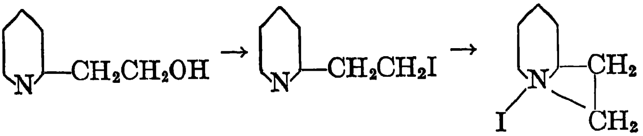
3,3′,8,10-tetramethylthiacarbocyanine salt



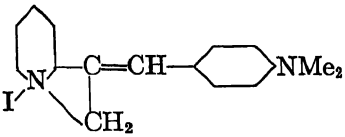
(75)

1′,3-diethyl-7-methylthia-2′-cyanine iodide by Brooker.[58] The latter noted the presence in some of the reaction mixtures of deeper-colored dyes of greater solubility.[59]

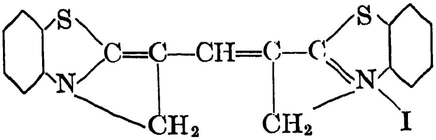
Quaternary salts with reactive methyl substituted in a different way were prepared by Schwarz.[60] For example, the alkine (76) is converted by phosphorus tri-iodide into (77), which on heating cyclizes into (78). The α-methylene in this salt is reactive and forms dyes, such as the benzylidene derivative (79). Similar reactions in the benzothiazole series yield dyes such as (80). DeSmet and Schwarz prepared salts such as (81), as indicated below, and these also yield cyanines;[61] while Dewael has prepared quaternary salts of the type of (82), and these yield cyanines such as (83).[62]



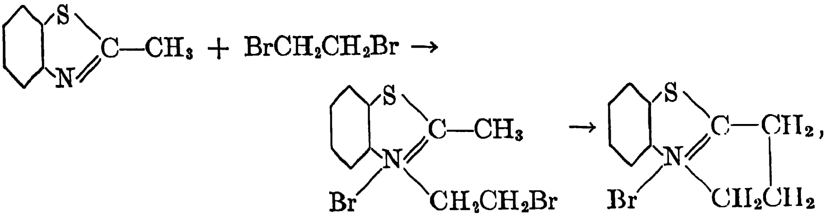
(76) (77) (78)



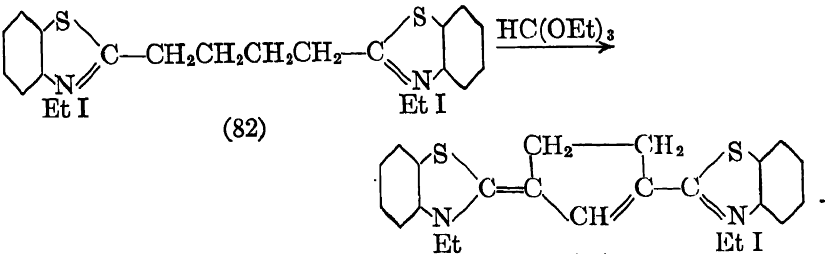
(79)



(80)



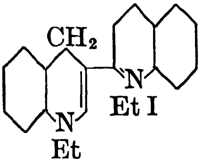
(81)



(83)

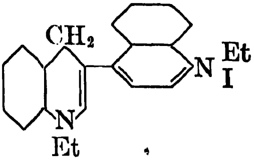
APOCYANINES

Kaufmann and Strübin obtained a mixture of two dyes, one yellow and the other reddish, called *xanthoapo-* and *erythroapocyanine*, respectively, by heating quinoline ethiodide with caustic alkali.[63] For these dyes, formulas (84) and (85) were suggested



1,1′-diethyl-3,2′-
apocyanine iodide
(xanthoapocyanine)

(84)



1,1′-diethyl-3,4′-
apocyanine iodide
(erythroapocyanine)

(85)

by König[64] and later confirmed experimentally by Mills and Ordish.[65]

These dyes are not important photographically but are interesting because the nuclei in them are joined together directly, rather than through a methine or polymethine bridge. Nevertheless, the two nitrogen atoms in each molecule are linked by a conjugated chain containing an uneven number of carbon atoms, and the apocyanines conform to the amidinium-ion system, like the rest of the cyanines. As usual, too, each type gives rise to two extreme resonance configurations, of which only one is given here in each case.

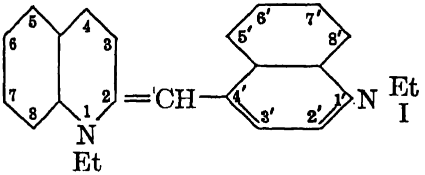
"WEIGHTING" THE CYANINE DYE MOLECULE

It has been shown that the absorption of a cyanine dye may be shifted either by lengthening or shortening the chain of carbon atoms between the two nuclei, this generally resulting in big shifts in absorption, or by replacing one or both of the nuclei by others with different color values, this resulting in big shifts or small, according to the nuclei changed.

A further method is known as *weighting* the molecule and consists of the introduction of substituent groups or atoms into either the nuclei or the chain connecting them, with, however, preservation of the general structure. This method is generally adopted if relatively slight shifts are required.

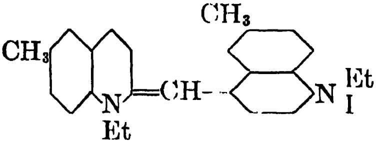
According to *Nietzki's Rule*, the color of a dye is deepened, *i.e.*, the absorption is shifted towards the red, the greater the molecular weight of substituent groups introduced; but this rule has many exceptions, and much depends upon the position in which the substituents are introduced. This device was especially used in the isocyanine series by E. König and his collaborators after unsubstituted dyes of this class had been found to be valuable sensitizers.[66] The series of absorptions shown in Figure 382 illustrates the magnitude of the effects obtained by weighting the isocyanine molecule with various substituents.

The introduction of methyl groups into the 6 and 6′ positions of 1,1′-diethyl-2,4′-cyanine iodide (*ethyl red*, (86)), which gives (87), shifts the absorption towards the red. Ethoxy groups in the 6 and 6′ positions (88) are more potent in their effect than methyl and cause a greater shift, and dimethylamino groups are



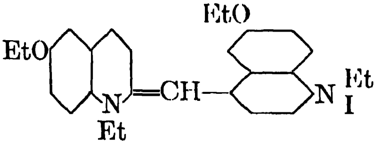
1,1′-diethyl-2,4′-cyanine iodide
(ethyl red)

(86)



1,1′-diethyl-6,6′-dimethyl-2,4′-cyanine
iodide (orthochrome T)

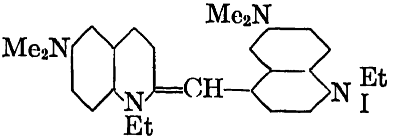
(87)



6,6′-diethoxy-1,1′-diethyl-2,4′-cyanine iodide
(pinachrome)

(88)

the most powerful of all (89). In practice, these dyes were very


(89)

6,6′-di(dimethylamino)-1,1′-diethyl-2,4′-cyanine iodide
(pinachrome violet)

useful sensitizers, and the names under which they were sold by the German dye makers are shown under the systematic names.

A somewhat different mode of weighting the dye molecule is by the attachment of benzene nuclei. This is especially effective in the *thiacarbocyanine* series, and the absorption spectra in Figure 383 show the results obtained. The addition of two benzene residues to (90), which gives (91), is seen to shift the absorption band strongly toward the red, while two benzene

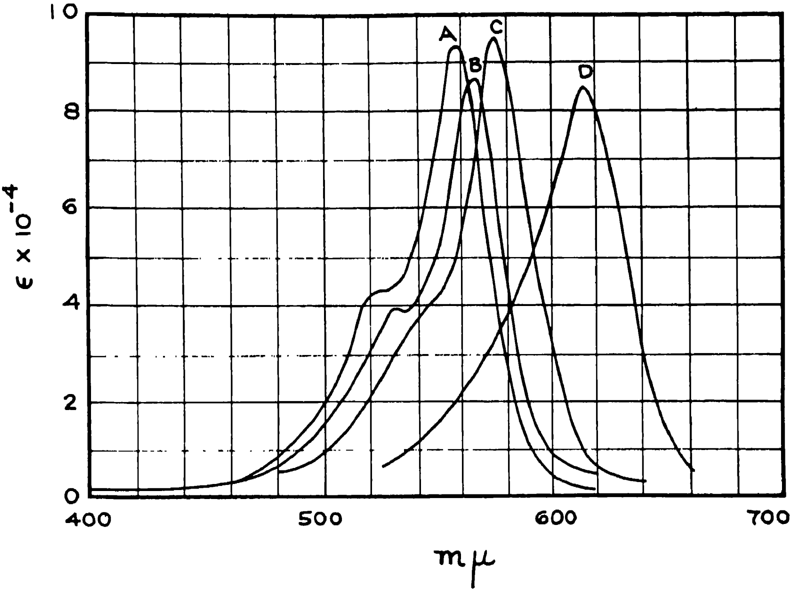
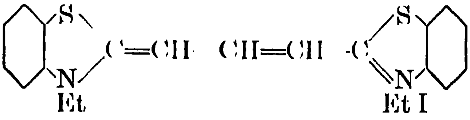
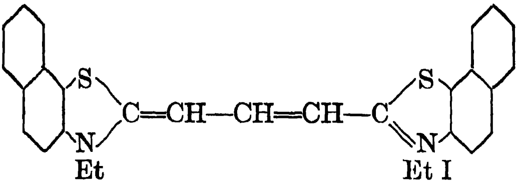


FIG. 382. Absorption spectra in methanol: *A*, ethyl red (formula (86)); *B*, orthochrome T (87); *C*, pinachrome (88); *D*, pinachrome violet (89).


(90)

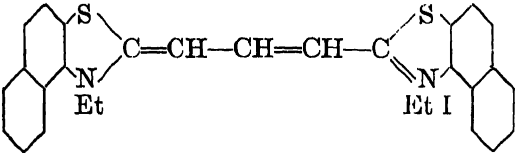
3,3′-diethylthiacarbocyanine iodide

rings affixed in different positions in the dye molecule, as shown in (92), have an additional effect. In general, the addition of



(91)

3,3′-diethyl-6,7; 6′,7′-dibenzothiacarbocyanine iodide



(92)

3,3′-diethyl-4,5; 4′,5′-dibenzothiacarbocyanine iodide

benzene rings in this way deepens the color of a dye, but in certain cases it produces either no alteration in λ_{max} or even a shift in absorption toward the violet.[67]

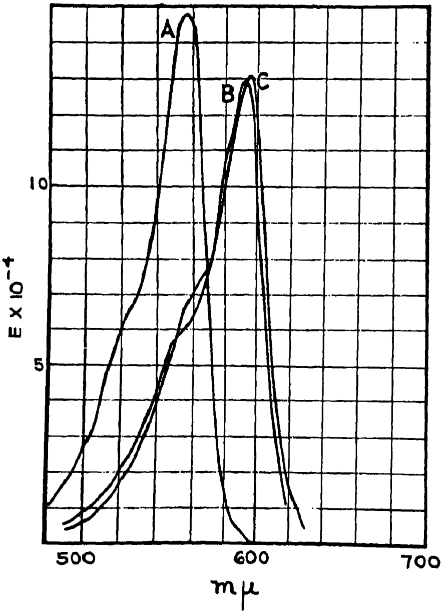


FIG. 383. Absorption spectra in methanol: *A*, formula (90); *B*, (91); and *C*, (92).

A further mode of weighting that has been closely studied, because many of the dyes are outstanding photographically, is the introduction of substituent groups into the central position of the three-carbon chain of carbocyanines, giving dyes with the bridge $=CH-C(G)=CH-$, in which G is the substituent group (p. 1010). Thus, in the thiacarbocyanine (90), the central hydrogen atom of the molecule has been replaced by the groups methyl, ethyl, propyl, *n*-butyl, *n*-amyl, benzyl, phenyl, and so forth;[68] but, rather surprisingly, the introduction of an alkyl group or of benzyl actually shifts the absorption toward the blue, methyl being the most effective, and phenyl produces only a slight shift toward the red. These effects are shown in Figure 384.

The methods followed in the preparation of dyes weighted with substituent groups are, in general, similar to those used for preparing the corresponding unsubstituted dyes; but the yields are often markedly affected by the introduction of substituents, and in some cases modified methods must be adopted. Thus, although a good yield of 3,3′-diethyl-9-methylthiacarbocyanine iodide ((90), but with the chain =CH—CMe=CH—) is obtained by the condensation of 2-methylbenzothiazole ethiodide with ethyl orthoacetate in the presence of pyridine, and the same method applied to 2-methyl-α-naphthothiazole ethiodide gives (91) (with =CH—CMe=CH—) but in lower yield, it fails completely with the isomeric salt 2-methyl-β-naphthothiazole ethiodide,[69] which would be expected to give (92) (but with =CH—CMe=CH—). However, the use of 2-methyl-β-naphthothiazole etho-p-toluenesulfonate in place of the iodide enables the desired dye to be obtained.[70]

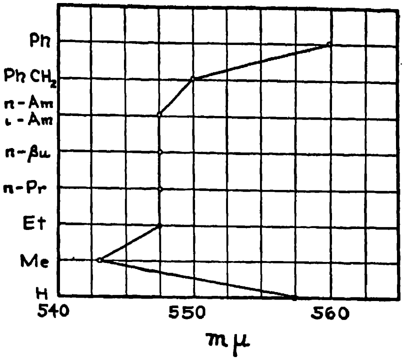
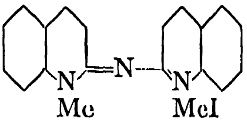


Fig. 384. Values of λ_{max} for a series of 3,3′-diethylthiacarbocyanine iodides of the structure shown in formula (90) but with various groups G in the carbocyanine chain, thus: =CH—CG=CH—.

AZACYANINES

It is possible to prepare cyanines in which a =CH— group in the methine or polymethine chain is replaced by =N—. Such a dye is called an *azacyanine*.[71] The first dye of this class (93)



(93)

1,1′-dimethyl-9-aza-2,2′-cyanine iodide

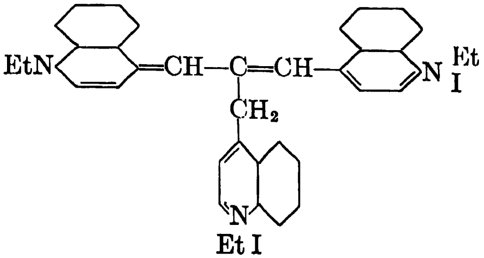
was prepared by Hamer.[72] A number of other azacyanines have been described[71] in which the two nuclei are linked directly through =N—. In all cases, they are lighter in color than the corresponding cyanines with =CH—.

In the carbocyanine series, one or more of the =CH— groups of the =CH—CH=CH— chain may be replaced by =N—. Thus, dyes with =N—CH=CH— are described by Kendall[73] and with =N—N=CH— by Fuchs and Grauaug[74] and Fisher and Hamer.[71] All of these are lighter in color than the corresponding carbocyanines with =CH—CH=CH—. Dyes with the chain =N—CH=N— are described by Fisher and Hamer and are very much lighter in color than the related carbocyanines. Kendall has pointed out that if the aza group =N— is introduced into the conjugated chain so that there are uneven numbers of carbon atoms between it and the terminal nitrogen atoms of the chain, the dye is a sensitizer; if the intervening carbon atoms are even in number, the dye is a desensitizer.[75]

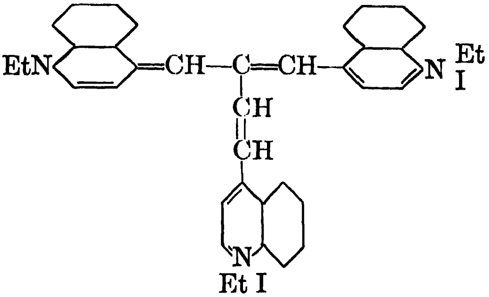
CYANINE DYES CONTAINING THREE NUCLEI

A few types of cyanine dyes containing three heterocyclic nuclei are known.

In 1925, H. T. Clarke, while preparing 1,1′-diethyl-4,4′-carbocyanine (kryptocyanine), found that a second dye was formed in smaller amount, which was less soluble and which absorbed and sensitized farther in the infrared than kryptocyanine.[76] This was called neocyanine and was investigated by Hamer,[77] who suggested formula (94) for it, according to which the molecule contained three nuclei and two acidic radicals; but the modified formula (95) was suggested in 1933.[78] A third formula (96),

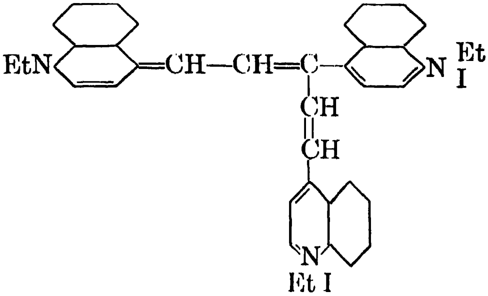


(94)



(95)

neocyanine ethiodide (?)



(96)

neocyanine ethiodide (?)

isomeric with (95), is regarded as more probable by W. König;[79] but the matter has not yet been decided unequivocally. The absorption of neocyanine is very similar in general shape to that of kryptocyanine, as shown in Figure 385.

Trinuclear dyes which, doubtless, have a similar bridge to neocyanine but contain three thiazole nuclei instead of three 4-quinoline nuclei are described in the patent literature,[80] and Ogata found that the preparation of other carbocyanines may be modified to yield the corresponding trinuclear neocyanine types.[81] That derived from benzothiazole, for example, is similarly deeper in color than the normal carbocyanine; and the absorption spectra are otherwise very similar in shape (Figure 386).

Members of a second group of trinuclear cyanines have been prepared independently by different workers,[82] a general method being the condensation of a quaternary salt containing reactive methyl with carbon tetrachloride or tetrabromide in the presence of alkali. This method of synthesis clearly indicates the nature of the linkage in these dyes as shown in that derived from lepi-

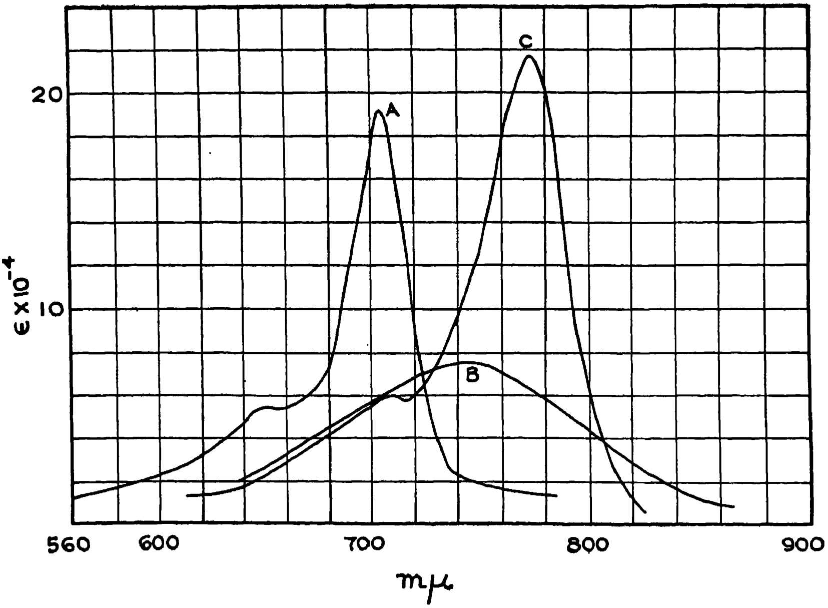


FIG. 385. Absorptions in methanol: *A*, 1,1′-diethyl-4,4′-carbocyanine iodide (kryptocyanine), formula (26); *B*, formula (97); *C*, neocyanine ethiodide, formula (95) or (96).

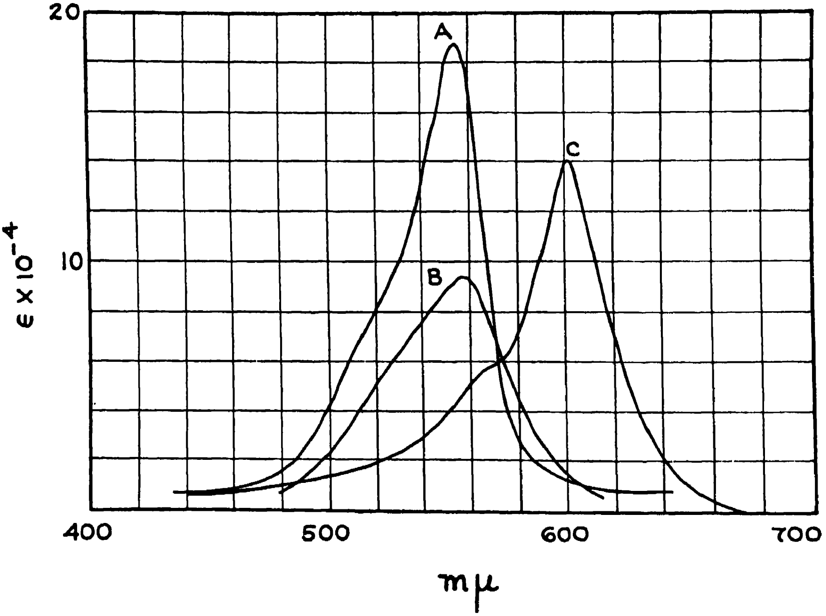
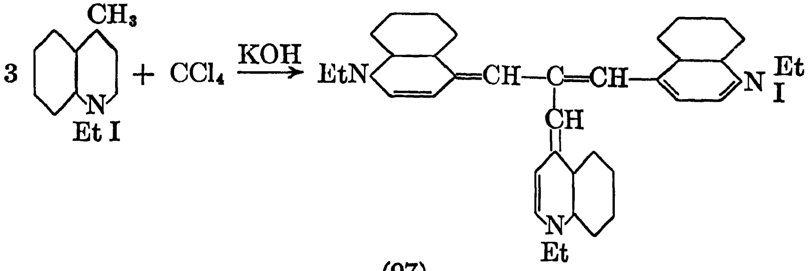


FIG. 386. Absorptions in methanol: *A*, 3,3′-dimethylthiacarbocyanine iodide, formula (90) but with Me groups in place of Et; *B*, formula (98); *C*, the neocyanine corresponding to *A*.

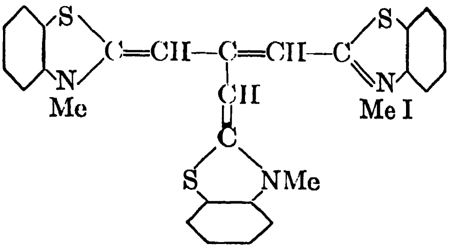
dine ethiodide (97). In this dye one anion is shared by the



(97)

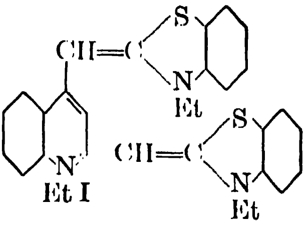
three nitrogen atoms, and there are three identical ways of writing the formula corresponding to three extreme structures between which the dye is a resonance hybrid.

The absorption spectrum of (98), which is a trinuclear dye of the type of (97) but contains three benzothiazole nuclei, is shown in Figure 386 (curve *B*).



(98)

Trinuclear cyanines of a third type were prepared by Brooker and Smith.[83] In them a quinoline nucleus is linked through the 2- position with a second heterocyclic nucleus and through the 4- position with a third, as shown in (99), in which these second and third nuclei are derived from benzothiazole. This dye is prepared by the condensation of 2-methylbenzothiazole etho-*p*-



(99)

toluenesulfonate (2 mols) with 2,4-diiodoquinoline ethiodide (p. 1007), and in it, as in (97) and (98), one acidic radical is shared by three nitrogen atoms, and there are consequently three ways of writing the formula, each corresponding to an extreme resonance state; but in (99), unlike (97) and (98), no two of the three extreme resonance configurations are the same, and in (99) the linkages present are characteristic of three distinct cyanine types, *i.e.*, thia-2′-cyanine, thia-4′-cyanine, and, in a sense, thiadicarbocyanine. The absorption curve is complex (Figure 387-B), consisting of two separate bands, which is ascribed to the co-existence in the molecule of the different modes of resonance enumerated, although a somewhat different interpretation is given by Lewis and Calvin.[13]

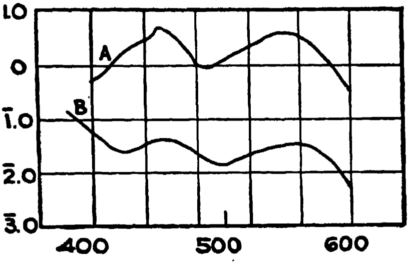


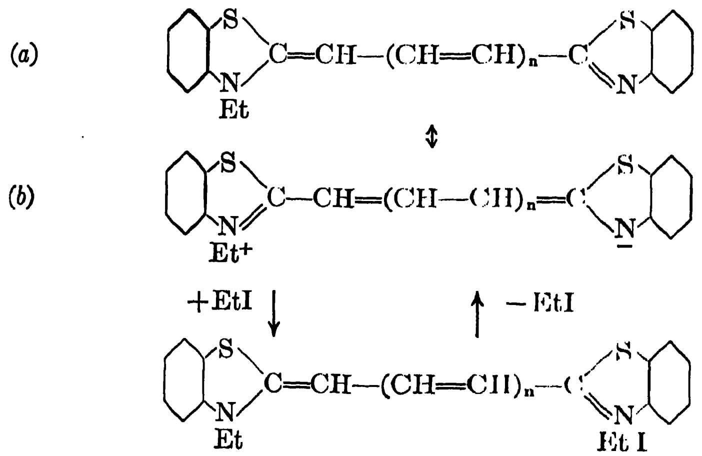
Fig. 387. *A*, absorption spectrum in methanol, formula (98); *B*, sensitizing spectrum of formula (98) in a silver chloride emulsion.

Dye (99) is a good sensitizer and provides an especially interesting example of the relation between absorption and sensitizing bands. If a silver chloride emulsion is sensitized with the dye, the sensitivity curve shows two distinct peaks, which are closely related to those of the absorption band (Figure 387-A).

BASES RELATED TO THE CYANINE DYES

The cyanines are complex quaternary salts, and removal of alkyl halide from the molecule should, theoretically, give bases capable of combining with alkyl halide to re-form the original cyanines.

Examples of both types of reaction are found in the literature. Thus, Mills in 1922[84] prepared the base (100) ($n = 0$), which by the addition of ethyl iodide yielded the cyanine (101) ($n = 0$); but many years elapsed before the reverse process was accomplished and Schwarz[85] prepared the base by heating the cyanine with a large excess of diethylaniline, the latter presumably combining with the ethyl iodide split off from the dye. This latter method has also been used to prepare the bases from the thiacarbo- and thiadicarbocyanines ($n = 1$ and 2, respectively), and



(100)

(101)

the absorptions of the three bases have been compared with those of the three cyanines.[9]

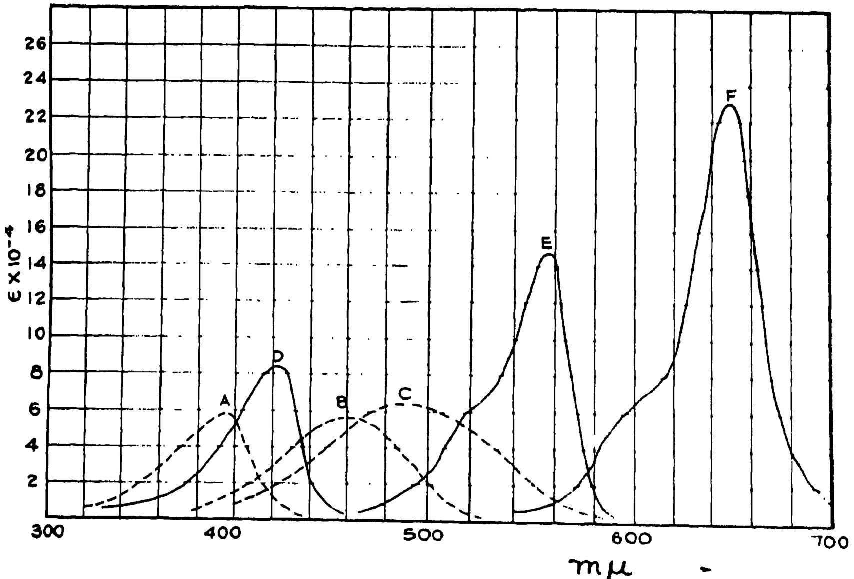


Fig. 388. Absorption spectra in methanol: A, B, C, formula (100), when $n = 0, 1, 2$, respectively; D, E, F, formula (101), when $n = 0, 1, 2$, respectively.

In each of these cases, a base is lighter in color than the cyanine of the same chain length (Figure 388). As has already been shown, increasing the length of the conjugated chain in the cyanines by the addition of vinylene produces large shifts in the absorption, but the corresponding shifts in the bases are less. The difference in λ_{max} between a base and the cyanine of the same chain length, therefore, increases as the series is ascended, *i.e.*, as the value of n in (100) and (101) increases. The figures for λ_{max} for the six compounds are given in the following table:

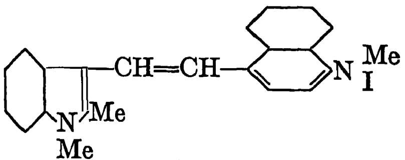
TABLE LXXXVI

Compound	*Absorption max. in mμ*	*Differences in mμ*
100, $n = 0$	396	
1	458	> 62
2	490	> 32
101, $n = 0$	423	
1	557	> 134
2	650	> 93

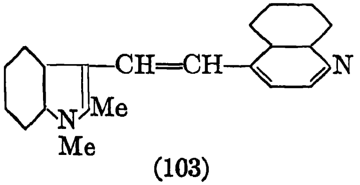
These relationships show clearly that the mere presence of a conjugated chain in a compound is not in itself sufficient to account for deep color, since the bases and the cyanines have conjugated chains of the same length for the same values of n but the cyanines are much the more deeply colored.

The difference in absorption between the two series of compounds may be accounted for, however, by use of the resonance theory.

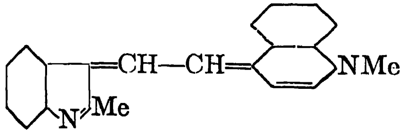
An unsymmetrical cyanine gives rise to two different bases, depending upon whether alkyl halide is removed from one or other of the nuclei. Thus, both the isomeric bases (103) and (104) may be considered to be derived from the dimethine cyanine (102) by removal of methyl iodide. The absorptions of



(102)



(103)

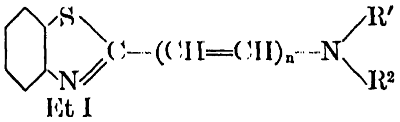


(104)

(103) and (104) are very different, however, (104) being by far the more deeply colored of the two and deeper in color, even, than (102). These facts, too, have been explained from the resonance standpoint; and it has been concluded that of isomers of the type of (103) and (104), the more deeply colored one will be that in which the alkyl group is attached to the nitrogen atom of the more basic nucleus. Other pairs of isomeric bases related to the cyanines have been prepared by Hamer,[86] and their relative colors seem to be in agreement with this rule.

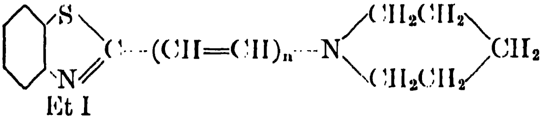
HEMICYANINES

Under this heading may be included a number of dyes conforming to the amidinium-ion system but in which only one nitrogen is situated in a heterocyclic ring and the conjugated chain passes through a portion of this ring. If the benzothiazole ring is selected as a typical heterocyclic ring, the hemicyanines may be exemplified by (105), in which R′ and R^2 are hydrogen, alkyl, or aryl and *n* = 0, 1, 2, 3, and so forth.

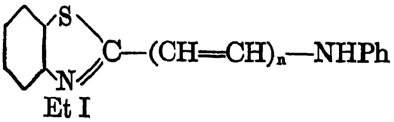


(105)

In general, these dyes may be prepared by treatment of a heterocyclic component of type *B* (p. 1005) with an aromatic or aliphatic amine containing replaceable hydrogen, and a number of these syntheses were worked out independently by Ogata[35] and White and Keyes.[87] If both R′ and R^2 are aliphatic residues, the intermediate, which may contain a reactive mercapto group or an acetanilido group, is condensed with the appropriate secondary aliphatic amine, *e.g.*, diethylamine, dibenzylamine, piperidine. With piperidine, the vinylene homologous series (106) (n = 0, 1, 2, 3) has been built up. If the reactive intermediates are condensed with primary aromatic amines, compounds such as the anilino series (107) (n = 0, 1, 2, 3) are formed.

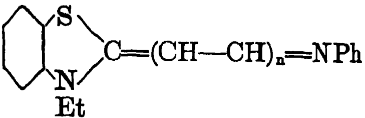


(106)

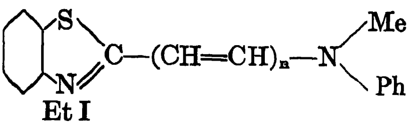


(107)

Upon treatment with alkali, these yield the anils (108), which readily combine with methyl iodide to yield the methylanilino hemicyanines (109), this method being generally applicable if R′ in (105) is aliphatic and R^2, aromatic.



(108)

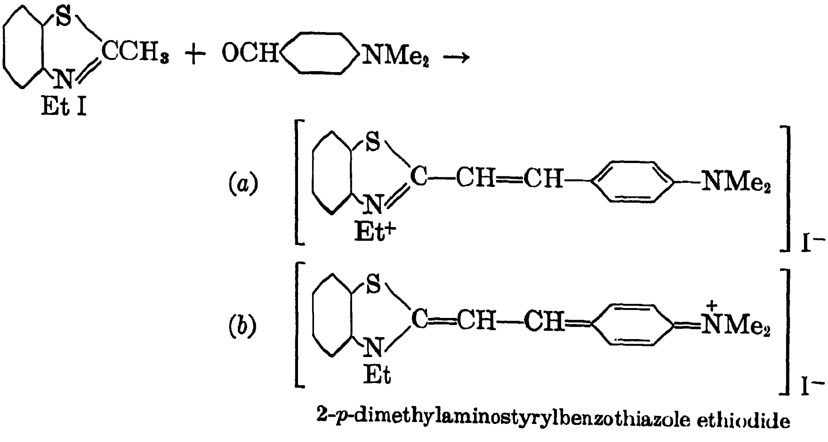


(109)

p-DIALKYLAMINOSTYRYL DYES

In the list of dyes conforming to the amidinium-ion type (p. 991), one (11) has one nitrogen atom in a heterocyclic nucleus, but the second nitrogen is not part of a ring system. This dye is, therefore, not a true cyanine and may be regarded as a hemicyanine. Dyes of this type generally possess sensitizing action, and a few are outstanding in this respect.

The general method of preparation is by condensation of the appropriate quaternary salt containing reactive methyl with a *p*-dialkylaminobenzaldehyde, usually under the influence of piperidine as a catalyst:[88]

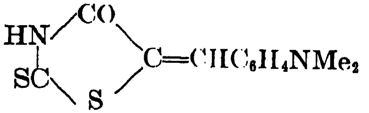


2-*p*-dimethylaminostyrylbenzothiazole ethiodide

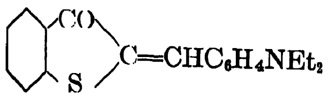
(110)

DYES CONTAINING THE AMIDE SYSTEM; THE MEROCYANINES

While searching for photographic sensitizing dyes of new types, Kendall and Brooker discovered independently that certain *p*-dialkylaminobenzylidene derivatives of compounds containing a methylene group activated by carbonyl were good sensitizers.[89] These compounds include, for example, 5-(*p*-dimethylaminobenzylidene)rhodanine (Feigl's reagent for silver) (111) and 2-*p*-diethylamino-3(2)-thianaphthenone (112). The



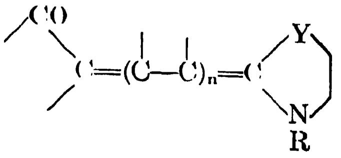
(111)



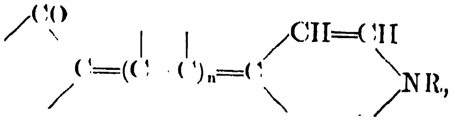
(112)

auxochromophore common to these dyes is the amide grouping $O{=}\overset{|}{C}{-}(\overset{|}{C}{=}\overset{|}{C})_n{-}N<$ (p. 989), and many other dyes containing this system have been prepared in which the N atom forms part of a heterocyclic ring, as in the cyanines.[90]

These dyes may be represented by one of the two general formulas (113) and (114), in which Y represents $O<$, $S<$, $Se<$, $Me_2C<$ or $—CH{=}CH—$, and R, alkyl. The dyes form vinyl-



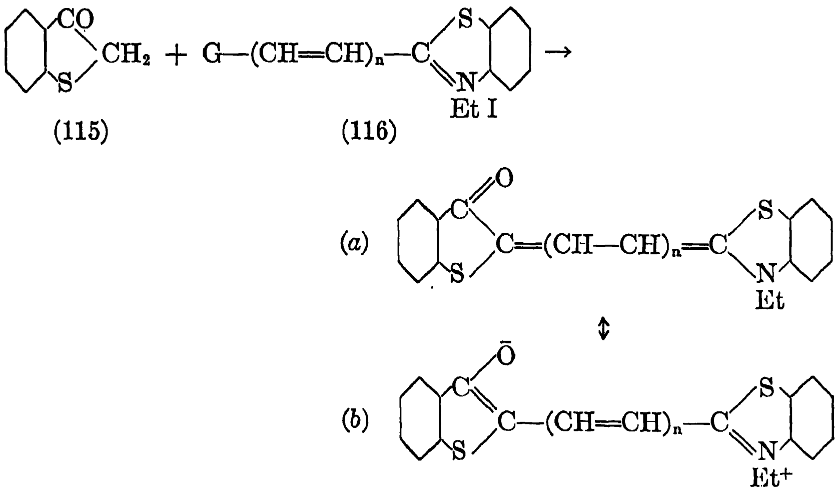
(113)



(114)

ene homologous series, so that n = 0, 1, 2, 3. Like (111) and (112), these dyes are derived from compounds containing the $—COCH_2—$ grouping, and this and the derived group $—CO—\overset{|}{C}{=}$ in the dyes themselves may form part of a ring system or chain. Since the new dyes contain a heterocyclic nucleus of the type found in the cyanines, the name *merocyanine* (Gk. *meros* = part, portion) for them was suggested by Hamer.

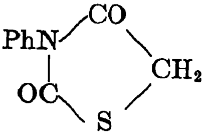
Whereas the cyanines are frequently formed by the condensation of an intermediate containing a heterocyclic nucleus with a heterocyclic quaternary salt containing reactive methyl, in the preparation of merocyanines the latter is replaced by a compound containing the $—COCH_2—$ group. For example, 3(2)-thianaphthenone (115) reacts with intermediates of the type of (116), such as (34) or (35), G representing a reactive negative atom or group. In the course of the reaction, G is eliminated together with a hydrogen atom of the reactive methylene group of (115), giving a mercaptan RSH, where G is a mercapto group, or acetanilide, where G is an acetanilido group. The acid radical of (116) is also eliminated with the second hydrogen of the methylene group of (115). The reactions are, therefore, usually carried out in the presence of a basic condensing agent, such as pyridine, triethylamine, or potassium carbonate, which serves to bind the acid eliminated.



(115) (116)

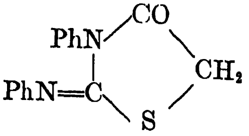
(117)

The number of compounds containing a reactive methylene group and capable of giving merocyanines is very great. Chain compounds such as acetyl acetone, ethyl malonate, ethyl acetoacetate, cyanoacetamide, benzoylacetonitrile, and nitromethane may be used; but more frequently cyclic compounds such as (115) and (118) to (124) are employed:



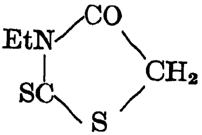
3-phenyl-2,4(3,5)-thiazoledione

(118)



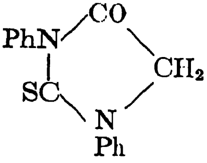
3-phenyl-2-phenylimino-4-thiazolidone

(119)



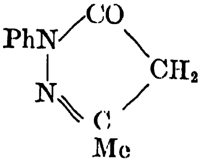
3-ethylrhodanine

(120)



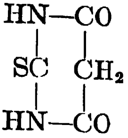
1,3-diphenyl-2-thiohydantoin

(121)



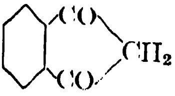
3-methyl-1-phenyl-5-pyrazolone

(122)



2-thiobarbituric acid

(123)



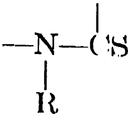
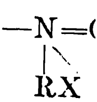
1,3-indandione

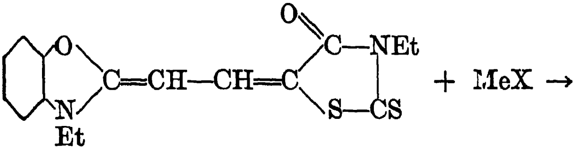
(124)

The number of heterocyclic nuclei of the type present in the cyanines that may be employed in the preparation of merocyanines is also considerable.

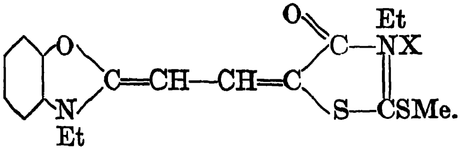
The merocyanines are neutral compounds and dissolve in non-polar as well as polar solvents, thereby differing from the cyanines, which are ionized in solution and, in general, are soluble only in polar solvents.

Complex Dyes Derived from the Merocyanines

It is known that compounds containing the grouping  $-\underset{R}{\underset{|}{N}}-\overset{|}{C}=S$ frequently combine with alkyl salts to give compounds with the grouping  $-\underset{RX}{\underset{|\diagdown}{N}}=\overset{|}{C}SAlk$, and it has been found that merocyanines containing this grouping combine with alkyl salts, *e.g.*, iodides or *p*-toluenesulfonates, to give alkylmercapto compounds:

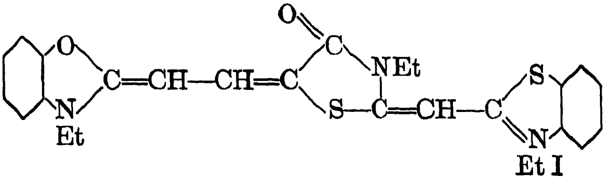


(125)

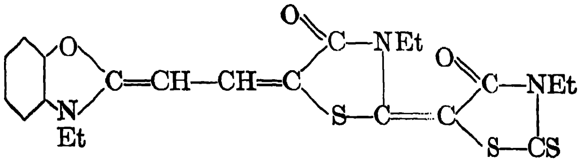


(126)

In these alkylmercapto compounds, the S-alkyl group is reactive, as it is in (34), and is capable of condensing with compounds containing reactive methyl or methylene to give complex dyes. Thus, on treatment with 2-methylbenzothiazole ethiodide in the presence of a base, (126) yields (127); and treatment with 3-ethylrhodanine yields (128). Reactions of this kind have been discovered independently by Kendall[91] and Brooker.

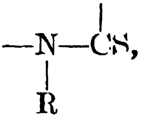


(127)



(128)

These complex dyes are deeper in color than the merocyanines from which they originate; but, in spite of the large number of possible auxo-chromophoric systems in (127) and (128), it is noteworthy that their absorption spectra (Figure 389) are no more complex than those of the parent dye (125) (which, itself, admittedly contains a number of possible auxo-chromophoric systems), so that apparently the absorption is produced by the molecule vibrating as a whole.

In dyes such as (127), which also contain the unit  $-\underset{\underset{R}{|}}{N}-\overset{|}{C}S$,

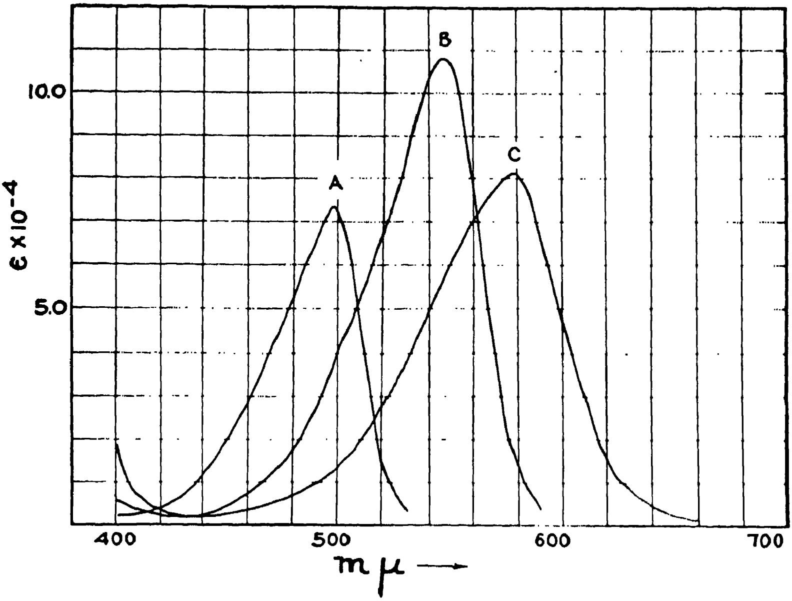
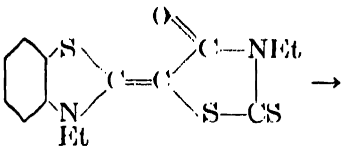
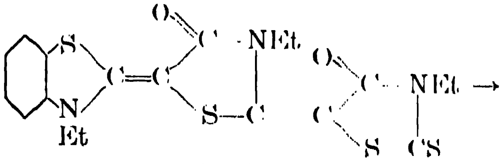


Fig. 389. Absorption spectra in pyridine: *A*, formula (125); *B*, (128); *C*, (127).

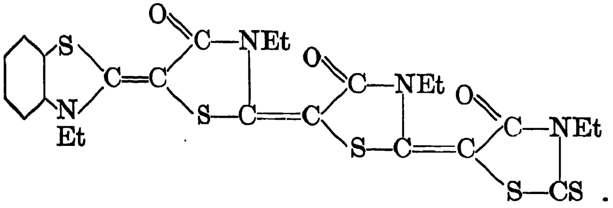
a repetition of the process is possible, and still more complex dyes may be evolved. Thus, the simple merocyanine (129)



(129)



(130)



(131)

yields (130), and this, in turn, yields (131); and still further additions are theoretically possible. However, as more nuclei are added to these dyes, the solubility diminishes, and the preparative steps become increasingly difficult.

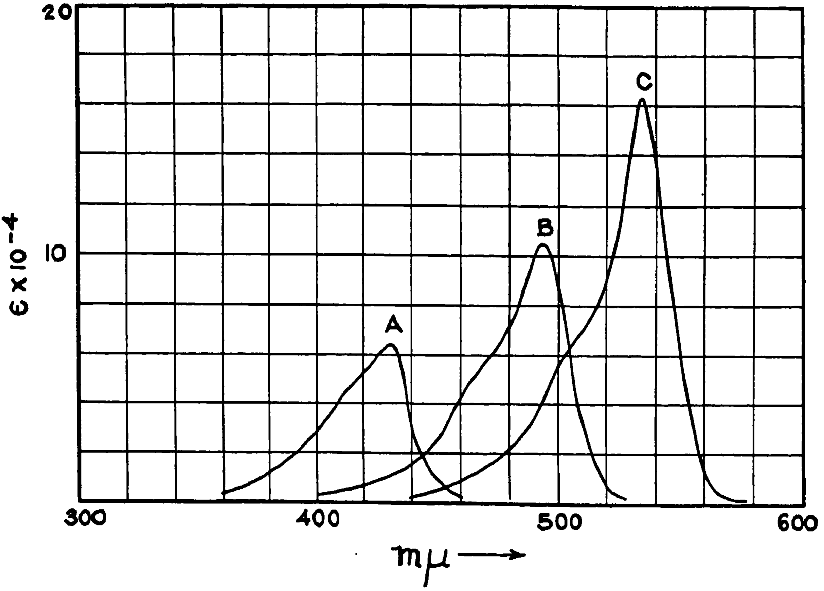


FIG. 390. Absorption spectra in pyridine: *A*, formula (129); *B*, (130); *C*, (131).

The addition of 3-ethylrhodanine nuclei to (129) deepens the color progressively (Figure 390); but, again, the curves are of a simple character.

DESENSITIZING DYES

Some dyes are used as desensitizers in photographic practice; their structure is studied in the following pages.

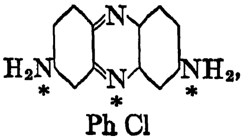
Desensitizers are used to decrease the sensitivity of photographic materials so that they may be developed in a relatively bright light. An ideal desensitizer should fulfill a number of requirements, which Hamer[92] formulates as follows: It should (1) rapidly and almost completely destroy the sensitivity of a film bathed in a dilute solution of it, (2) not attack the latent image, (3) not cause fog, (4) be conveniently soluble in water, (5) be stable in both the solid state and solution, (6) not be destroyed or precipitated by the developer, (7) not interfere with development or fixation, (8) preferably be colorless or, if colored, nonstaining, and (9) be nonpoisonous.

While no substances are known which fulfill all these requirements, a number of compounds have proved useful in practice. In 1901, Lüppo-Cramer[93] called attention to the desensitizing action of most developers; and in 1920[94] he pointed out that the normal sensitivity of photographic emulsions was reduced to a small fraction after they had been bathed for about one minute in a solution of diaminophenol hydrochloride, although no reduction in the latent image resulted from this treatment. He recognized that this desensitizing was due to traces of oxidation products formed by the autoxidation of the developer. Continuing his experiments, Lüppo-Cramer[95] found that phenosafranine, a well-known red dye, was a very powerful desensitizer and as a pre-bath enabled development to be carried out in the presence of a considerable amount of light. The dye could also be used in the developer, the addition of one part in 20,000 enabling the plate to be examined in a bright light after only one minute's development. Serious objections to phenosafranine are the very persistent red stain that it leaves on the plate and its restraining effect on development. Lüppo-Cramer pointed out that desensitizing dyes such as phenosafranine are oxidizing in character.[95c] He suggested that the oxidizing power is strong enough to inhibit further formation of latent image but insufficient under normal conditions to attack that already present. This is supported by the fact that such desensitizers destroy the latent image in the presence of increased concentrations of soluble bromide. In terms of the Gurney-Mott theory, this means that the ideal desensitizer should trap the electrons released by the absorption of light (Chapter IV) but should not be able to extract electrons from silver atoms. The suggestion of Lüppo-Cramer given above receives considerable support from the work of Blau and Wambacher.[96] They have shown that the characteristic desensitizing action of dyes such as phenosafranine and pinakryptol yellow (141) is somewhat inhibited if the plates are exposed in the absence of oxygen either by working in a vacuum or in an atmosphere of pure dry nitrogen. The dye therefore appears to behave as a photochemical catalyst in the desensitizing process, the principal part being played by the oxygen of the air.

While some dyes which produce optical sensitizing desensitize, and some desensitizers, such as phenosafranine itself, sensitize optically, the fundamental difference between the two phenomena is that, whereas the sensitizing effect of a dye is intimately bound up with its spectral absorption, such a relation does not exist between desensitization and absorption. If applied to a panchromatic plate, phenosafranine, for example, desensitizes in the blue and red spectral regions, which it transmits, as well as in the green, which it absorbs. Furthermore, many colorless desensitizers are known.

The general observation has been made that if desensitizers are applied to color-sensitized emulsions, the spectral region of extra-sensitivity is preferentially attacked; and this is ascribed to an exchange reaction whereby the sensitizing dye adsorbed to the silver halide grain is replaced by the desensitizer.

Phenosafranine is commonly represented by formula (132),

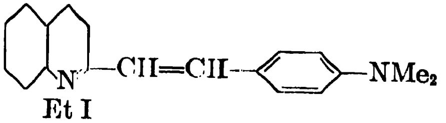


(132)

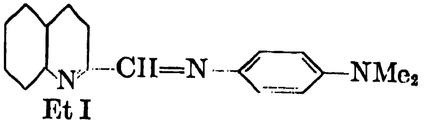
and the desensitization is not seriously reduced by alkyl substituents introduced into the phenazine nucleus or the amino groups, or by the replacement of the phenyl group in >NPh by alkyl.

In formula (132), three of the nitrogen atoms, indicated by asterisks, can share the cationic charge, whereas the fourth is necessarily uncharged; it is this atom which is doubtless largely responsible for the behavior of the dye as a desensitizer, since a nitrogen similarly linked is characteristic of a great many desensitizing dyes.

Formulas (133) and (134) are the formulas of two dyes, (133) being a styryl and (134) the corresponding anil, respectively. The styryl is a sensitizer, while anils of the type of formula (134) are powerful desensitizers. Kendall[97] noted that in (134) the



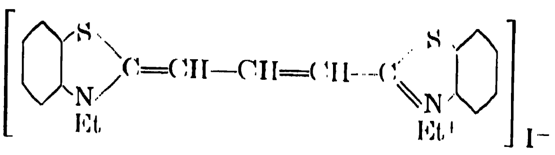
(133)



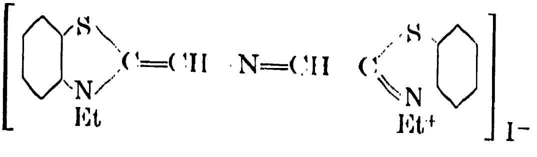
(134)

nitrogen atom within the chain is separated from those at the ends by even numbers of carbon atoms, and he associated this fact with the desensitizing character of the dye. He showed further that if a nitrogen atom replaces a =CH— group of a conjugated chain in a dye such as (133), but in such a way that it is separated from the terminal nitrogens by *uneven* numbers of carbon atoms, the dye is no longer a desensitizer but usually a sensitizer. This feature is brought out very clearly in the following comparisons:

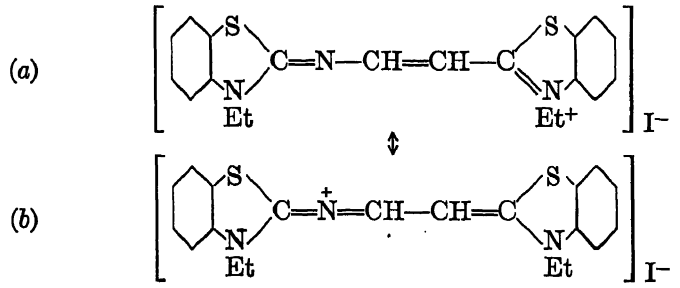
A =CH— group in the conjugated chain of the strongly sensitizing thiacarbocyanine dye (135) may be replaced by nitrogen to give either (136) or (137). In (136), the central nitrogen



(135)

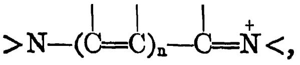


(136)



(137)

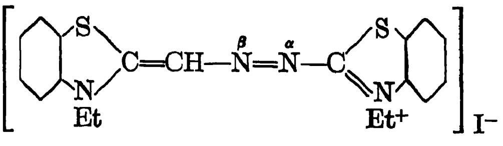
atom is separated from the terminal nitrogens by two carbon atoms on each side; the dye is a strong desensitizer and, in addition, is devoid of sensitizing properties.* In (137), the nitrogen in the chain is separated from the terminal nitrogens by one carbon atom on one side and by three on the other, and the dye is a sensitizer without marked desensitizing properties. In (136), the central nitrogen cannot share the quaternary charge with the terminal nitrogen atoms, as is the case with the fourth nitrogen atom in the molecule of phenosafranine (132); but in (137) the nitrogen atom in the chain is so located that it can share the charge, as shown in (137*b*). This serves to divide the originally long chromophoric chain in (135) into two shorter fragments. The dye is accordingly considerably lighter in color than (135); but these two fragments individually conform to the amidinium-ion formula which is characteristic of cyanines in



$$>N-(\overset{|}{C}=\overset{|}{C})_n-\overset{|}{C}=\overset{+}{N}<,$$

general (p. 992), so that it is not surprising that it sensitizes.

It is now possible to understand the action of dyes such as (138), which is a diazacarbocyanine of a type originally described by Fuchs and Grauaug.[74] The nitrogen atom marked α is simi-



(138)

larly located to that in (137) and should not, therefore, confer desensitizing properties. The β nitrogen atom, on the other hand, is similarly placed to that in (136), and this confers desensitizing properties. Actually, the dye is a strong desensitizer; but, as already stated, the two properties are not necessarily incompatible, and the dye also confers weak sensitivity to green.

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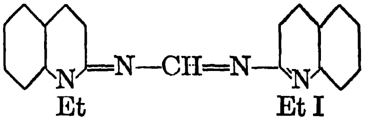
* Hitherto unpublished observations from the Kodak Research Laboratories.

In the diazacarbocyanine (139), both of the nitrogen atoms of

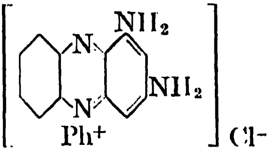


(139)

the =N—CH=N— are linked similarly, with respect to the terminal atoms, to that in the chain =N—CH=CH— in (137); and in (139) all four nitrogen atoms share the ammonium charge, and none has a permanently unshared electron pair. This dye would not, therefore, be expected to desensitize strongly, nor, in fact, does it; and it also weakly sensitizes a chloride emulsion. The dimethyl compound (Me in place of Et in (139)) is described as photographically inert.

Although anils such as (134) are rapidly destroyed by the sulfite in the developer, it is interesting that the desensitization conferred by their use in a preliminary bath persists when the film is transferred to the developer. This is ascribed to increased stability of the dye-silver halide adsorption complex compared with that of the dye itself.

One of the most useful of all desensitizing dyes is pinakryptol green (140). In this dye, which, it is interesting to note, is



(140)

isomeric with phenosafranine (132),[98] the quaternary charge is shared by three of the four nitrogen atoms, the second phenazine nitrogen retaining its tertiary state throughout. This dull green dye is powerful in its action and is effective either as a preliminary bath or in the developer. It does not stain as badly as phenosafranine and, hence, has been very widely used.

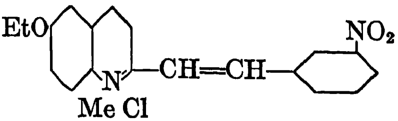
Many dyes of the thiazine series, such as methylene blue, show desensitizing action, although often accompanied by fog.

The oxazines behave similarly, but neither of these series has so far yielded a good practical desensitizer.

Chrysoidine desensitizes powerfully but inhibits development to a marked degree.[99] In this dye, the charge is again shared by three of the four nitrogen atoms of the molecule.

In spite of the fact that the triphenylmethane dyes are not characterized by a system in which a permanently trivalent nitrogen atom lies in a resonating chain, many of the dyes of this group desensitize powerfully, although sometimes with fog; *e.g.*, malachite green, brilliant green, so that the grouping referred to cannot be the only one that confers desensitizing properties. Triphenylmethane dyes are of no practical use, as their effect is destroyed by the sulfite in the developer.

A group of colorless or nearly colorless compounds was investigated by Schuloff[100] and includes several closely related compounds that have been sold under the name of pinakryptol yellow. One of these is represented by (141), but slight variations have been made. These compounds are styryl derivatives, and the best results are obtained with a nitro group in the *o*, *m*, or *p* position, as in (141); but there is considerable desensitizing effect even in the absence of a nitro group.



(141)

A number of patents[101] describe desensitizers derived from anthraquinone, which may be used in either a preliminary bath or the developer. These are acidic derivatives; and in some of the earlier of these, such as anthraquinone-2-sulfonic acid and 1-chloroanthraquinone-2-carboxylic acid, the interesting claim is made that their action is due to their forming very insoluble salts with the basic cyanine dyes, withdrawing them from adsorption on the silver halide grains. It follows that such desensitizers would be effective only for desensitizing color-sensitized materials and then only if basic dyes were used; it is, in fact, stated that they are ineffective if used for emulsions sensitized with erythrosine and that, in any case, development must be by red light, the ordinary blue sensitivity of the emulsion not being affected. In later patents, however, compounds such as anthraquinone-2-carbonyltauride, the anthraquinone sarcoside, and the sulfonate are claimed to desensitize ortho- and panchromatic emulsions indiscriminately; and development may be carried out, after a brief interval, with a bright green or yellow light.

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17*a*. Reference 22 (Chapter XXIII, p. 984).

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CHAPTER XXV

THE MECHANISM OF OPTICAL SENSITIZING

Although the literature includes many suggestions as to the mechanism of sensitizing, only in very recent years has any real advance in the understanding of it been made.[1] Vogel and Eder showed that some kind of combination of the dye with the silver halide is essential to sensitizing, but the nature of this was not understood. Eder suggested that vibrations produced in the dye molecule by the absorption of light are transferred to the silver halide and effect its decomposition. Abney suggested that the dye is decomposed by light and that the decomposition products reduce the silver halides.

The investigations which throw light upon the mechanism of sensitizing deal with

A. The chemical structure of the sensitizing dyes and their molecular state in solution.
B. The adsorption of the sensitizing dye to silver halide and the relation of the absorption spectrum of the dyed halide to that of the dye in solution.
C. The probable structure of the layer of adsorbed dye.
D. The photolytic efficiency of the dyed halide.
E. The mechanism of transfer by which the absorption of light by the adsorbed dye layer results in the liberation of electrons in the silver halide crystal.

THE STRUCTURE AND MOLECULAR STATE OF SENSITIZING DYES

The chemical constitution of the sensitizing dyes is discussed in Chapter XXIV. With the exception of erythrosine, a xanthone dye, whose structure is shown at 5, p. 990, those most commonly used are polymethine dyes corresponding to the general structure 3, p. 988, and characterized by a conjugate chain to which their absorption for light is due. Sheppard[2] showed that the absorption spectra of sensitizing dyes may vary with the solvent. In the case of organic solvents, the differences are small, being chiefly the shift of the maximum of absorption toward longer wave lengths as the refractive index of the solvent increases. The differences in absorption for organic and aqueous solutions, however, are very considerable. A number of isocyanines show one strong absorption band, with a shoulder on the short wave length side which was more or less emphasized in different solvents but in water assumed an importance equal to or greater than the primary maximum at longer wave lengths (Figure 391). Further, the relative strength of the two bands was altered by alkali in water but not in alcohol. The behavior is reversible, and there was no evidence of a chemical change of the molecule. With pinacyanol (a red-sensitizing dye, Ch. XXIII, p. 972) in water, a new band was observed in the shorter wave lengths (*ca.* 505 mμ) which did not appear in organic solvents. Upon raising the temperature of the water solution, this band disappeared and was replaced by the band for organic solvents, this being reversed upon lowering the temperature. Sheppard concluded that the changes were due to reversible aggregation of the dye molecules—the organic spectra representing monomolecular solutions and the aqueous (at low temperatures), polymolecular dispersions which at higher concentrations produced colloid particles, the latter being coagulated by electrolytes. This conclusion was supported by ultramicroscopic and other observations.

For many years, little attention was paid to the state of aggregation of dyes in solution, although the matter is of importance for the dyeing of textiles and other applications. Reference was made at times to certain dye solutions being "colloidal"; but there was little systematic study of these systems till about 1931, when Robinson and his collaborators[3] commenced an important series of studies on "the nature of the aqueous solutions of dyes." In 1934, the Faraday Society held a symposium on "Colloidal Electrolytes,"[4] which included several important contributions relating to dyes.

The measurement of the diffusivity of dyes in solution can be applied to the determination of the state of aggregation by means of the Stokes-Einstein equation, though care is necessary to avoid errors due to the shape of the particles and their entrainment in the more rapid migration of the smaller ions present.[5] Using this method, Sheppard found that in dilute solutions containing low concentrations of bromide the particles of cyanine

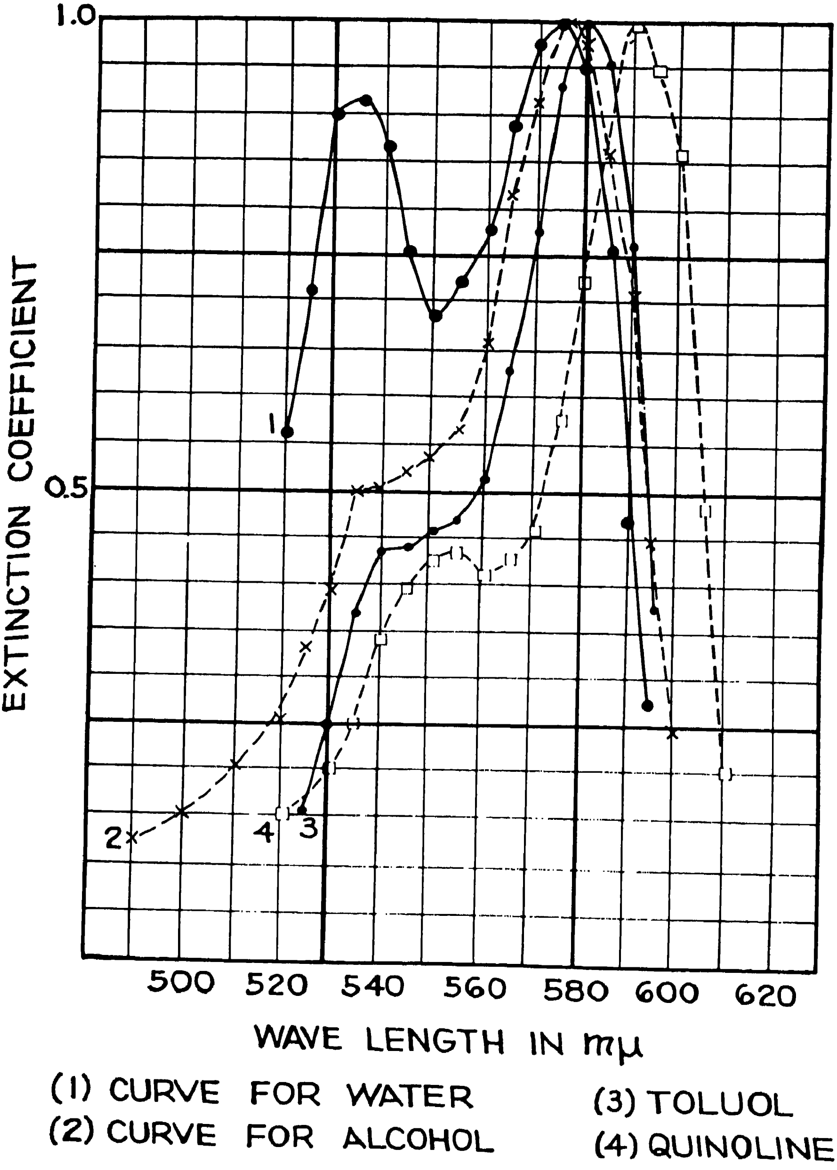


Fig. 391. Effect of the solvent on the absorption spectrum of a cyanine dye.

dyes showed a degree of aggregation corresponding to a few molecules only, from which he concluded that under the conditions used for sensitizing, the dye is molecularly dispersed. This does not preclude aggregated states being formed upon adsorption, which would favor such a condition.

The changes of absorption spectra of the polymethine dyes which had been studied by Sheppard in 1908 were investigated by Scheibe[6] and his co-workers. This work indicated that marked changes occur in the absorption spectra, amounting to relative suppression of one band (in the visible spectrum) and the appearance of new bands, either in the shorter or longer wave lengths, which Scheibe ascribes to what he terms the "reversible polymerization" of the dye molecules or, rather, of the dye cation. This does not differ greatly from Sheppard's conclusion that such changes are produced by "the reversible aggregation of dye molecules," but Scheibe and his co-workers followed the question in much greater detail. For pinacyanol, Scheibe's results were qualitatively similar to Sheppard's, but the positions of the bands in the spectrum were somewhat different, possibly owing to a difference in the composition of the commercial dye.

Diethyl pseudocyanine chloride was studied by Scheibe[7] and Jelley.[8] Both observed the production in water at 20° C. and concentrations of *ca.* 0.1×10^{-2} molar of a very intense, sharp band in the yellow which is not shown in alcohol (Figure 392). Scheibe associated the appearance of this band with the formation of a "highly polymerized form" (150–500). The degree of association decreases with rising temperature and decreasing concentration to about 100–180 molecular. That the dye is highly polymerized is also indicated by the very rapid increase of viscosity till jellies are produced. Jelley also observed the sharp band at 573–574 mμ in solutions of the pseudocyanine; the system gave very strong resonance fluorescence. But whereas Scheibe attributes the effect to highly polymerized forms, Jelley originally suggested that it was a molecular spectrum, distinct from ionic-molecular solution spectra. The high polymerization forms of Scheibe, Jelley considers, from streaming bi-refringence and other evidence, to be a nematic phase of threadlike aggregates which pass on aging into true crystallites.

His (unpublished) results on the nematic phase in a number of cyanines indicate that hydration of the dye is an essential factor in the formation of the aggregates but that the nematic state does not necessarily have a sharp absorption band. The weight of the evidence, including the data on the state of the

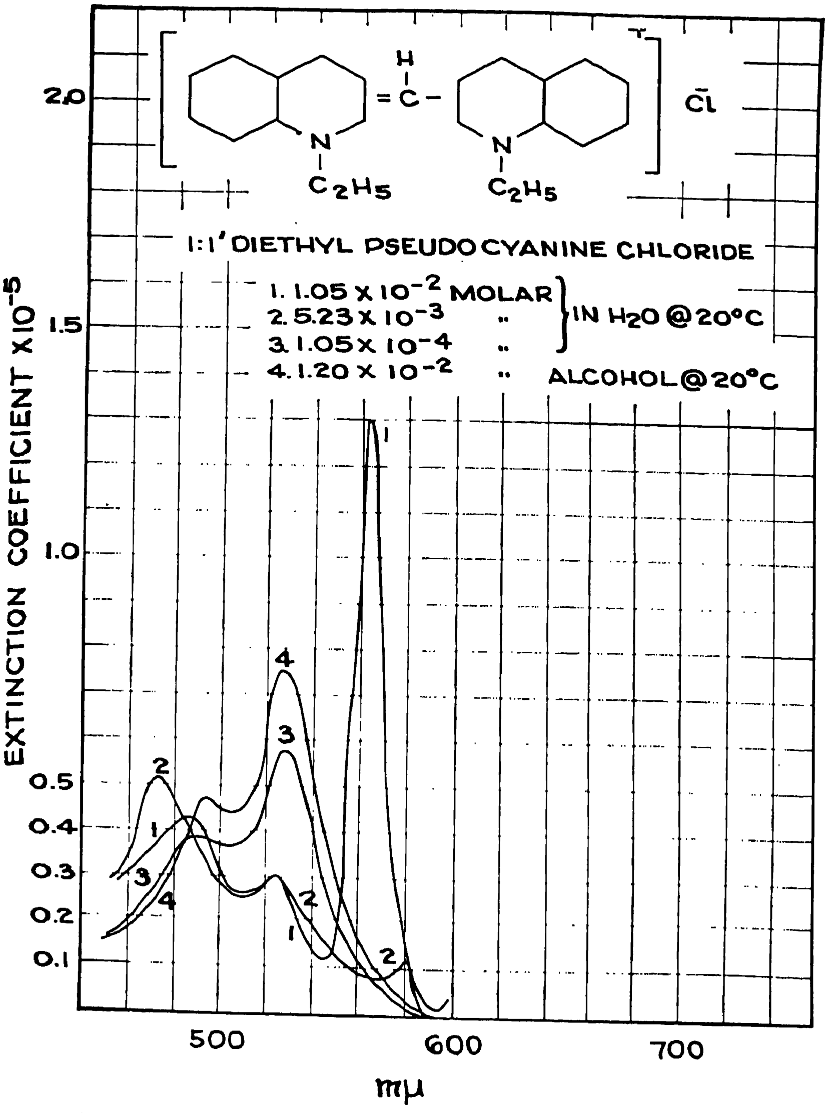


FIG. 392. Absorption spectrum of pseudocyanine chloride.

adsorbed dye on the silver halide, is in favor of the view that the new absorption bands are the result of definite arrangement of the dye molecules in the aggregates, which produces a new absorbing system. The absorption is, therefore, relatively independent of the number of molecules in the polymer, in contrast to Scheibe's hypothesis, which accounts both for longer and shorter wave lengths of the new bands by polymerization.

The reversible formation of higher polymers in water solution by way of dimer formation was observed by Ecker[9] in an extensive study of various quinoline dyes. He also confirmed Scheibe's result that in mixtures of dyes these polymers may contain different elements. The tendency to polymerize, however, varies strongly from dye to dye: A substitution in the ring may decrease the concentration needed for polymerization by as much as one hundred times.

THE RELATION OF THE SENSITIZING SPECTRA TO THE ABSORPTION SPECTRA

It was early realized that while the sensitizing spectra shown by dyed silver halides were related to the absorption spectra of the dyes in solution, they were not identical with them.[2] It was believed that the sensitizing spectra would be found identical with the absorption spectra of the dyes as adsorbed to the silver halides, but accurate measurements to prove this were difficult to make.

Leermakers, Carroll, and Staud[10] in 1937 showed that the sensitizing spectrum corresponds precisely to the absorption spectrum of the dyed silver halide, *i.e.*, of the adsorbed dye. This advance was made possible by measurements of the reflection spectra (spectral distribution of reflected light) of the dyed silver halides, using the rapidly operating photoelectric spectrophotometer of A. Hardy. Particularly cogent examples are furnished by Leermakers.[11] Figure 393, which represents a high-speed panchromatic emulsion, shows that the sensitivity curve follows the absorption curve closely and that the differences between the sensitivity and absorption maxima in the red are within experimental error. The data show that for this emulsion the sensitivity as measured is directly proportional to the amount of light absorbed. The sensitizing dyes used in these emulsions do not contribute appreciable absorption to the dyed silver halide grain at λ400 mμ, so that for this emulsion proportionality be-

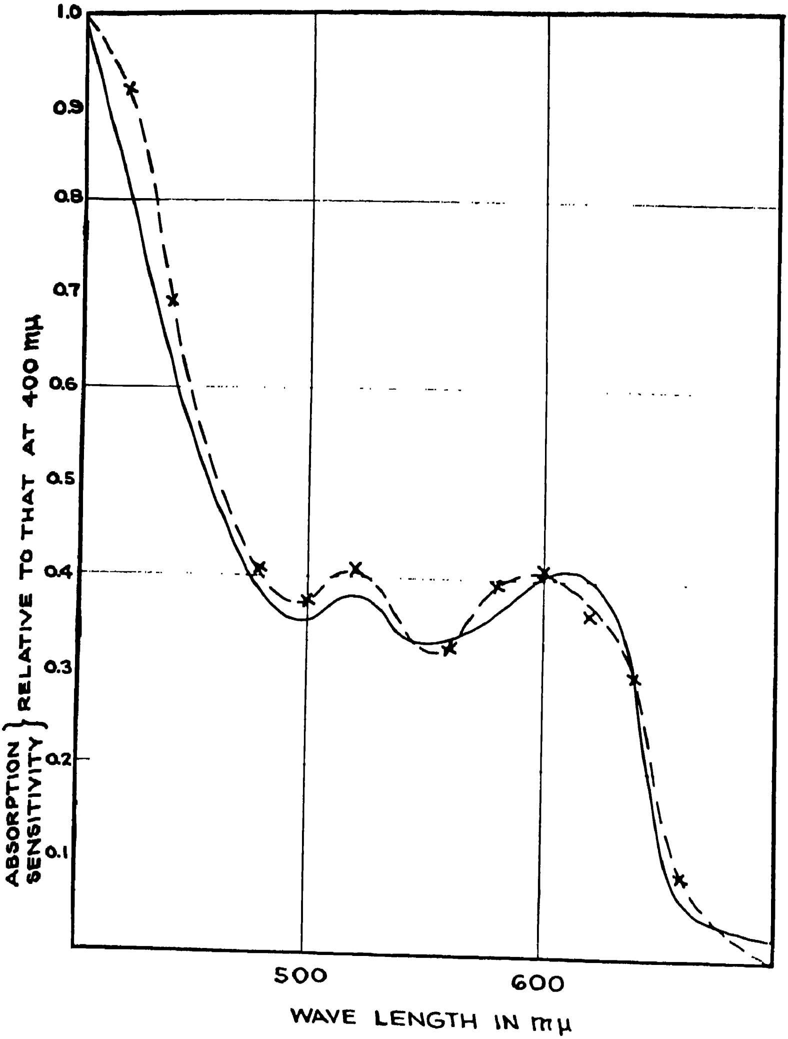


FIG. 393. Parallelism between absorption and sensitivity in a panchromatic material: *Solid line*, relative absorption; *broken line*, relative sensitivity.

tween absorption and sensitivity holds for spectral regions where the light is absorbed by the silver halide alone, and where it is absorbed by the adsorbed dye or by the dye-silver halide complex.

An interesting example of the relation of sensitizing to light absorption is shown by erythrosine. This is added to the emulsion in the form of sodium erythrosinate, of which the absorption

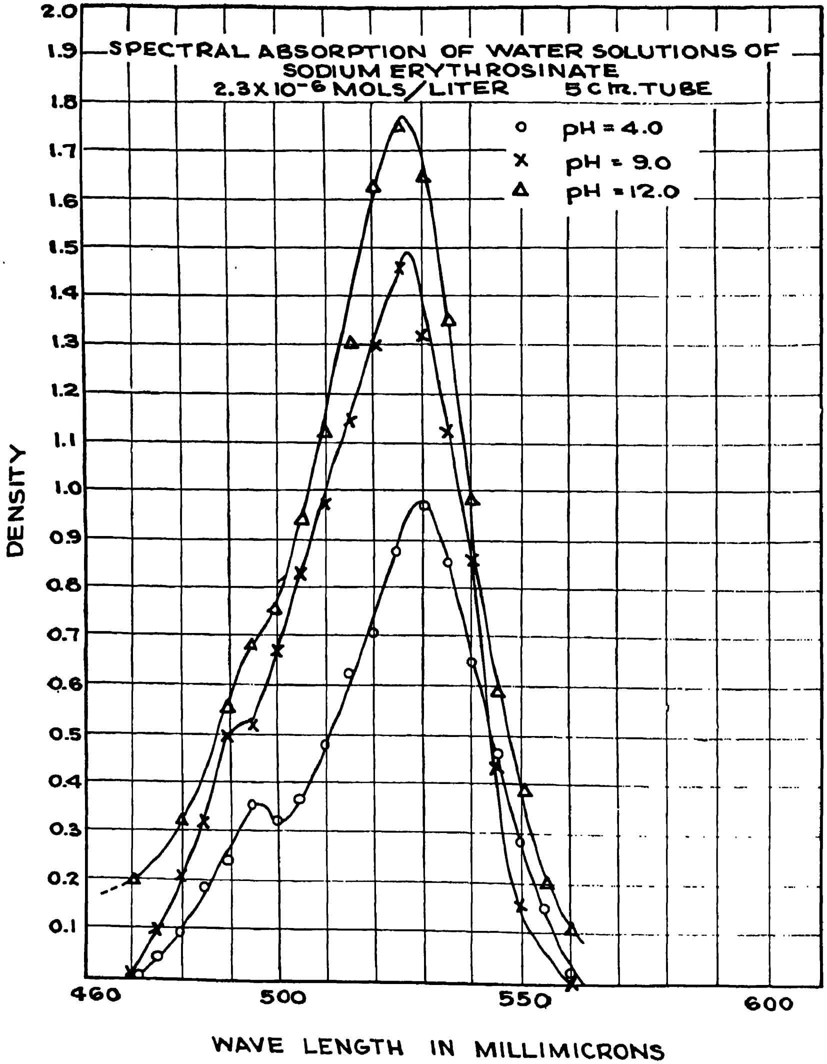
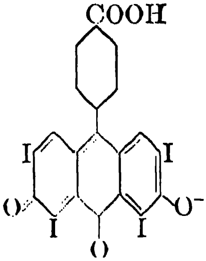


FIG. 394. Absorption spectrum of sodium erythrosinate.

spectrum is shown in Figure 394. The reflection spectrum of dyed silver bromide and the sensitizing spectrum deviate considerably from this, but they agree closely with the absorption spectrum of silver erythrosinate dispersed in gelatin.* In the dispersion, the silver erythrosinate is shown by examination with X rays to be in the solid state. It is evident, therefore, that in silver erythrosinate the anion is especially strongly affected by the cation, as pointed out by Fajans[13] and Frankenburger.[14] There does not seem to be a direct solvent for this substance; ammonia, pyridine, and amines dissolve it with dissociation of the silver ion and restoration of the spectrum of sodium erythrosinate. Its solubility in water is 5.8×10^{-6}—less than that of silver chloride although greater than that of silver bromide. Schwarz[15] showed that (*a*) the esterification of the carboxyl



(1)

group of erythrosine (1) does not destroy sensitizing power, (*b*) the removal of carboxyl does not do so, and (*c*) esterification of the phenolic OH *does* destroy sensitizing. Hence, it is by means of the resonating system $\text{O}{=}(\overset{|}{\text{C}})_{2n+1}\text{—O}^- \leftrightarrow \text{O}^-\text{—}(\overset{|}{\text{C}})_{2n+1}{=}\text{O}$ that the dye is adsorbed to the silver ion, a condition resembling that of the cyanines which are adsorbed to the halide ions by the system $>\overset{+}{\text{N}}{=}(\overset{|}{\text{C}})_{2n+1}\text{—N}< \leftrightarrow >\text{N—}\overset{|}{\text{C}}_{(2n+1)}{=}\overset{+}{\text{N}}<$. Schwarz points out that the gain in sensitizing power from fluoresceine → dibromfluoresceine → di-iodofluoresceine → tetraiodofluoresceine (erythrosine) is correlated with the decreasing solubility of the silver compounds of these dyes. The hydrophile carboxyl group probably accounts for the incomplete or reversible character of erythrosine adsorption to silver halides.

The merocyanines have the resonating system

$$>\text{N}\text{—}(\overset{|}{\text{C}})_{2n+1}{=}\text{O} \leftrightarrow >\overset{+}{\text{N}}{=}(\overset{|}{\text{C}})_{2n+1}\text{—O}^-$$

and differ further from the cyanines in that they are not salts of bases. The available data indicate that their sensitizing curves also correspond to the absorption curves of the compounds formed with silver.

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* Eder[12] concluded that the maximum absorption of an emulsion dyed with erythrosine corresponds to the maximum of sensitization, but his work was limited by the difficulty of measuring the absorption of silver halides.

THE ADSORPTION OF THE SENSITIZING DYES TO SILVER HALIDE

The first quantitative studies of the adsorption of sensitizing dyes to silver halide were made in 1928 by Sheppard and Crouch.[16] They measured the amount of dye removed from a solution as a function of the residual concentration of the dye in the solution. The measurement can be made either by following spectrophotometrically the loss of dye from the solution when shaken up with silver halide or by the extraction of the dye from the dyed silver halide.

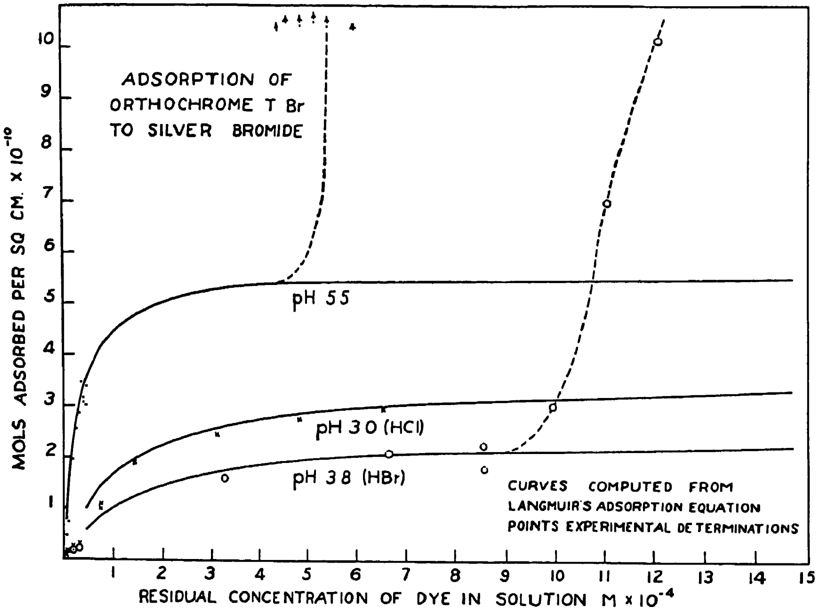


Fig. 395. Relation between the concentration of a cyanine and its adsorption to silver bromide.

A typical curve from the results obtained by Sheppard and Crouch is shown in Figure 395, in which the adsorption of the cyanine dye orthochrome T is plotted against the concentration of the dye solution. The dye adsorbed increases with the concentration of the solution until a first stage of saturation is reached, represented by the horizontal or "plateau" portion of the curve. This is followed by further adsorption, shown by the ascent of the curve as the concentration increases. The results up to the first stage of saturation can be represented by Langmuir's equation[17] for the adsorption of gases in a monomolecular layer. Assuming this for saturation, Sheppard and Crouch calculated that for a monomolecular layer of the dye, every molecule covered about three bromide ions of the surface of the crystals of silver bromide. In orthochrome T, the larger part of the molecule consists of the dye cation D^+; the lesser, the anion Br^-. Hence, Sheppard and Crouch concluded that the adsorption consists effectively of the electrostatic attraction of the dye cation D^+ for an external bromide anion of the silver bromide lattice. Similar conditions would obtain, of course, for silver chloride and silver iodide. On the other hand, with so-called *acid* dyes, of the type of eosine and erythrosine, the erythrosine *anion* is held, primarily by electrostatic attraction, to a silver cation of a silver halide lattice. Sheppard, Lambert, and Keenan's[18] experiments on the effects of halide and silver ions, respectively, on these two classes of dyes (basic and acid) confirmed these conceptions.

The interpretation as adsorption isotherms of curves such as those observed by Sheppard and Crouch for orthochrome T involves reversibility of the adsorption process, and this is also implicit in the Langmuir equation for the isotherm. This means that the silver halide saturated with the dye should release it to water. But Heisenberg[19] found that the adsorption of a dye of this type from water was complete, and similar results were observed by Leermakers, Carroll, and Staud,[20] who found that in the range of concentrations useful for sensitization, no unadsorbed dye could be detected, although a rapidly increasing amount appeared when the optimum concentration was exceeded. The behavior of adsorbed dyes toward solvents was studied by Sheppard, Lambert, and Walker.[21] A silver halide sol, *e.g.*, a stable suspension of silver bromide particles, was prepared as by Iljina and Bokinik[22] and stabilized by a sufficient excess of bromide ions. If this was titrated with a dilute aqueous solution of one of several polymethine dyes, *e.g.*, pinacyanol, after the addition of a certain amount, the silver halide and the dye were precipitated. The positively charged dye particles neutralize the negatively charged silver halide and cause mutual coagulation. But the phenomenon deserves closer examination, particularly in view of the repeptization by excess dye solution. Without detailing all the collateral evidence, the following gives a more exact picture of the adsorption of the polymethine dyes. The diagram of the structure of a cyanine dye in Figure 396 shows that the molecule has a polar (hydrophile) and a nonpolar (organophile) aspect. The former is conditioned by the quaternary nitrogen atom or, more exactly, by the residual affinity of the key atoms of the resonance chain for the anion. Roughly speaking, the solubility of the dyes in water is due to the polar, ionizable part of the molecule although, as presently noted, this solubility is never large. The solubility in organic, particularly nonpolar, solvents is due to the cyclic nuclei and their side substituents.

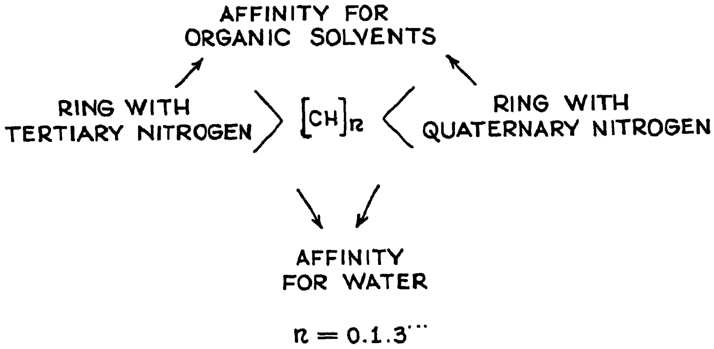

AFFINITY FOR ORGANIC SOLVENTS
RING WITH TERTIARY NITROGEN
[CH]n
RING WITH QUATERNARY NITROGEN
AFFINITY FOR WATER
n = 0.1.3˙˙˙

FIG. 396. Affinity diagram of a cyanine dye.

The adsorption of the polymethine (cyanine) dyes to polar solids, such as the silver halides, results in the fixation of the polar aspect of the molecule to the lattice of the crystals, the nonpolar organophile portion being exposed to the medium. The orientation of the adsorbed dye molecules is discussed later, but it appears that where optimum sensitizing is produced, the surface is covered with the leaf-like molecules piled edgeways in as close packing as is compatible with their own structure and the structure of the crystal to form a "parallel piled" or edge-on monomolecular layer. The new surface of the crystal (or crystallite, for hydrosols) has no hold upon water, but there is an attraction between the organophile parts of these surface-oriented molecules, so that colliding particles aggregate and precipitate. This stage corresponds to primary saturation and may be roughly represented, in section, by Figure 397.

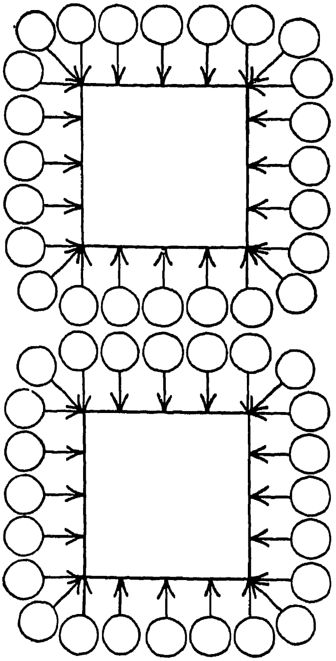


FIG. 397. Orientation of dye molecules to silver halide.

The primary saturation for the polymethine dyes may be determined in two ways: (1) with a hydrosol of silver halide by titration with dye solution to the point of precipitation or (2) with a suspension of silver halide grain in weak gelatin solution (silver halide emulsion) by shaking with equal volumes of dye solutions of varying concentrations until apparent equilibrium is reached, separating the grains centrifugally, and determining the residual dye in the solution and that adsorbed to the silver halide. The technique for the determination as developed by Sheppard and Crouch consists in extracting the dye from the solution of silver halide in thiosulfate with an organic solvent so that the optical density at the absorption maximum can be measured spectrophotometrically. Sheppard and Crouch used chloroform for extraction, but a higher partition (practically complete extraction) can be obtained with butyl alcohol.

Experiments show that while the adsorption of these dyes to silver halide is very rapid in plain water, it is retarded by the presence of gelatin, the rate of adsorption diminishing with the concentration of gelatin (Figure 398). Consequently, according to the time which elapses before measurement, the concentration of gelatin, and the temperature, a series of apparent adsorption isotherms might be obtained (Figure 399). The dyes can be extracted to some extent from the silver bromide with alcoholic solvents and even with gelatin but show no tendency to dis-

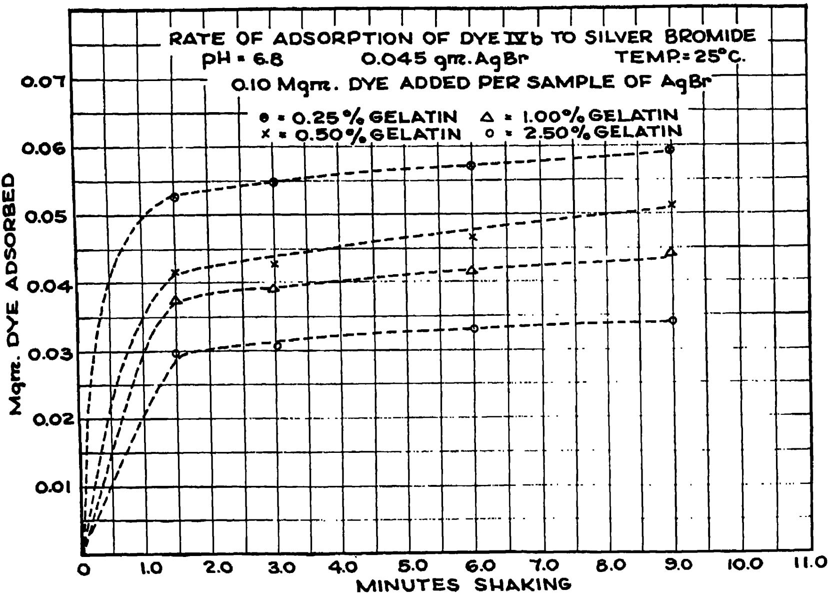


Fig. 398. Effect of gelatin on the adsorption of dye to silver bromide.

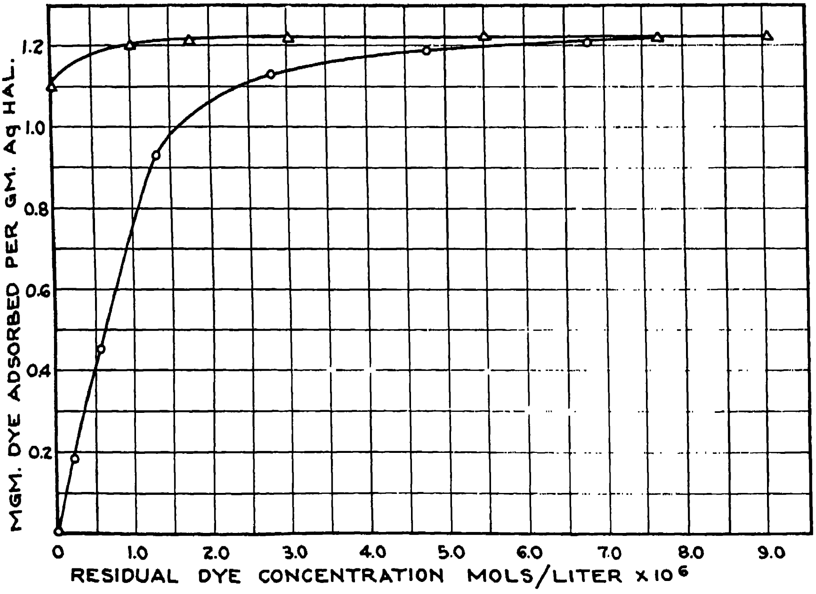


Fig. 399. Adsorption of dye to silver bromide.

charge in water. Since the dyes do not discharge from the silver halide to water, the adsorption process is irreversible. The fact that adsorption up to the saturation stage agrees with that given by Langmuir's equation is, therefore, a coincidence. Nevertheless, the horizontal portion of the curves corresponds to a true saturation level, which may be followed by a clearly marked second level, as shown in Figure 400. The adsorption density here corresponds to the formation of a second monolayer of dye molecules. Although the primary level tends to pass into a further stage, this does not always clearly indicate the formation of a true second monolayer.

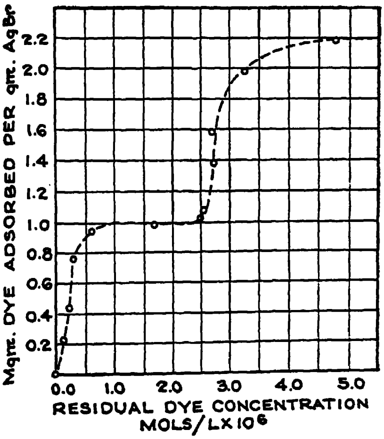


FIG. 400. Adsorption of dye showing two levels of saturation.

The conditions resulting in complete adsorption of the dye in the first layer need not hold for the second, where the polar groups of the molecules may be more exposed to the solvent. This agrees with the experimental observation of a rapid increase in unadsorbed dye if a certain concentration is exceeded. The state of adsorption of the dye is reflected in the sensitization which it produces. The total optical sensitization produced by a given dye passes through a maximum as concentration is increased. If absorption of light by the dye follows Beer's law, it will increase rapidly at low concentration and then approach 100 per cent asymptotically. Sensitivity actually tends to follow the first part of the absorption curve, but a marked desensitization replaces the expected flat portion at high concentrations. Typical results are given by Figures 401 and 402 (Leermakers, Carroll, and Staud), illustrating changes in sensitivity and contrast of three spectral regions with changing dye concentration. The sensitivity in the region of silver bromide absorption (blue filter) remains practically constant up to the concentration at which the other curves (red and green filter exposures) pass through their maxima. It then decreases as sharply as the

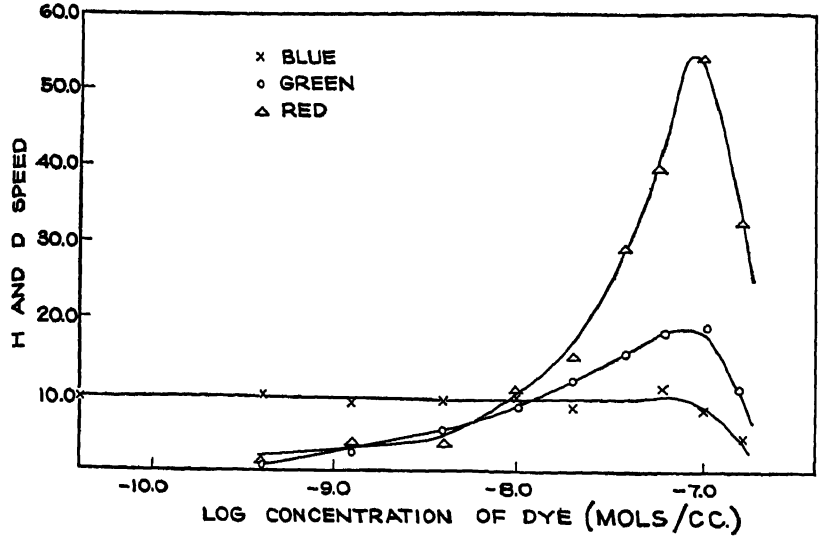


FIG. 401. Change of sensitivity with dye concentration.

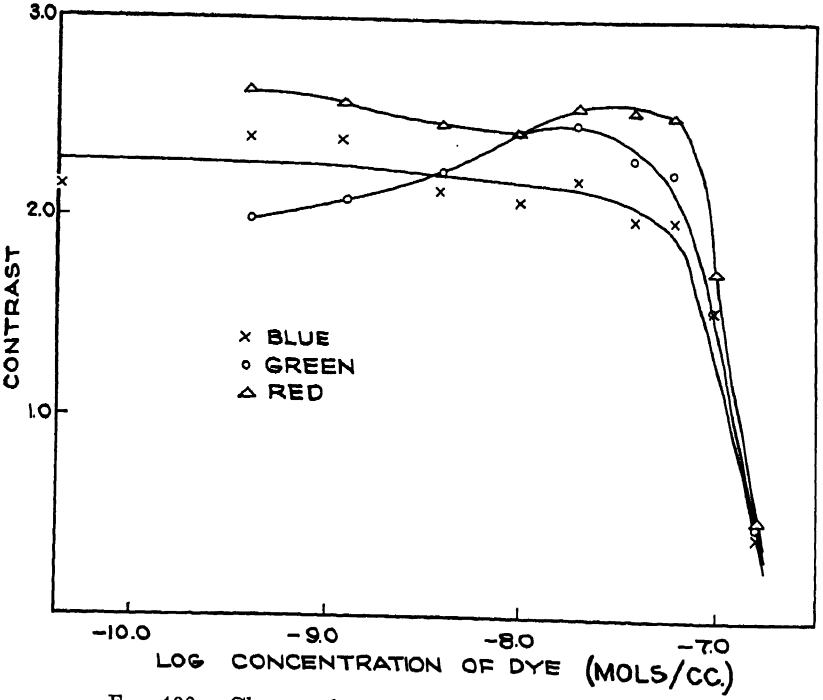


FIG. 402. Change of contrast with dye concentration.

others. The contrast in all regions falls rapidly at the same point. The dye used, a dibenzothiacarbocyanine, is completely adsorbed to the grains up to the optimum concentration. That a monomolecular layer of dye corresponds approximately to optimal sensitization was shown also by Eggert and Biltz.[23]

Proof that optimum sensitization corresponds to a definite condition of the surface is given by the following table, quoted from Leermakers, Carroll, and Staud. Seven emulsions, of both neutral and ammoniacal types, having a considerable range of grain size, were found to have a constant surface concentration at optimum sensitization. The concentration for the dibenzothiacarbocyanine I is slightly lower than for the thiacarbocyanine II and still lower is that for the thiadicarbocyanine III, the order following the relative sizes of the molecules. The values given correspond to about one molecule of dye I or II per ten bromide ions on the surface.

TABLE LXXXVII

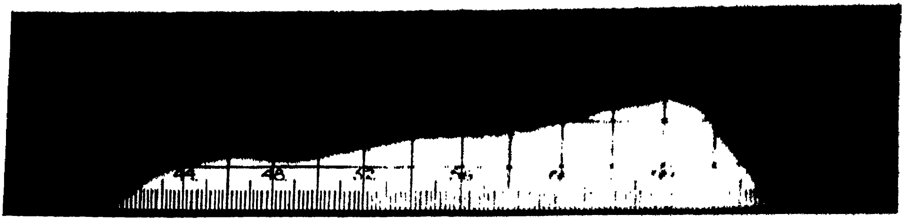
Surface Concentration of Dye for Optimum Sensitization

Emulsion	*Surface* cm^2/cm^3	*Dye*	*Optimum Concentration moles/cc. emul.* $\times 10^8$	$\frac{\textit{Moles Dye}}{cm^2\ \textit{surface}} \times 10^{11}$
1	400	I	3.6	9.0
2	480		3.8	7.9
3	580		5.2	9.0
4	660		6.0	9.1
5	840		7.2	8.6
6	950		9.0	9.4
7	1080		12.0	11.1
1	400	II	4.4	11.0
3	580		6.3	10.9
4	660		8.0	12.1
6	950		11.2	11.8
7	1080		12.6	11.6
1	400	III	1.9	4.8
3	580		2.3	4.0
4	660		2.9	4.4
6	950		4.8	5.0
7	1080		4.8	4.4

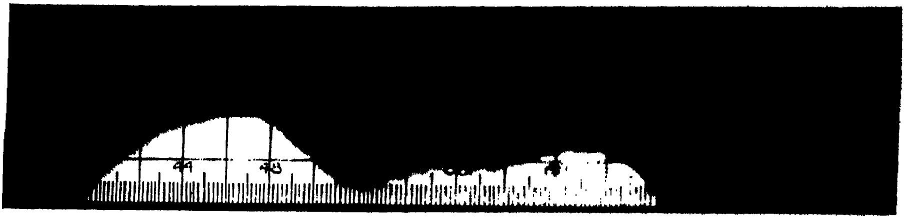
Since the amount of dye adsorbed at optimum sensitization increases with decreasing grain size or increasing specific surface, the capacity of fine-grained emulsions for strong sensitization is at once explained. The absorption of light at 400 mμ by a normal film coating is of the order of 80 per cent. In the region of optical sensitization, it rarely exceeds 50 per cent in spite of the exceptionally high absorption coefficients of cyanine dyes. The discovery of dyes having equal effectiveness and higher absorption might produce approximately uniform sensitivity throughout the visible spectrum.

If two or more dyes are used, sensitization by each is affected by the presence of the other. Since both are adsorbed to the silver halide surface, the most common result is a mutual interference. However, in some cases,[24] the sensitization by two dyes is greater than the sum of their separate effects (Chapter XXIII, p. 975). Red sensitization by dye A may, for instance, be increased by the addition of dye B, which sensitizes for green; or if A and B sensitize for the same region, A + B may sensitize more strongly than any concentration of either dye separately. This is known as *supersensitization* and is distinguished from *hypersensitization* produced by bathing the coated emulsion with ammonia or other solutions. The spectral absorption of one of the dyes on the silver halide may be changed by the presence of the other, supersensitization being not unusual among dyes which have more than one type of sensitization. In some cases, spectral absorption is unchanged, and the supersensitization can be described only as an improvement in the efficiency of latent-image formation for a given amount of energy absorbed by the dye.

The data of Leermakers, Carroll, and Staud show that sensitization may correspond to more than one of the types of spectral absorption characteristic of a dye. Two of their dyes give quite different spectrograms at low and high concentrations (Figures 403, 404). In each case, the sensitization at sufficiently low concentration corresponds to the absorption of silver bromide dyed from an alcoholic solution of the dye; the maximum of the curve is displaced from that of the alcohol solution and is broadened, but it seems reasonable to assume that it is characteristic of an unaggregated form of the adsorbed dye. At higher concentrations, the distribution of spectral sensitivity is profoundly modified by the appearance of a new maximum; in each case, sensitization then corresponds well with the absorption

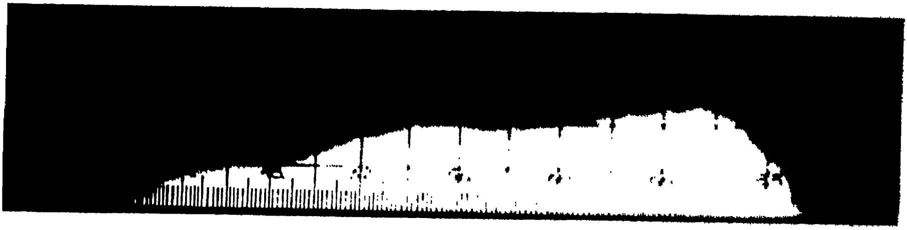


5 mg. dye per 100 cc. emulsion

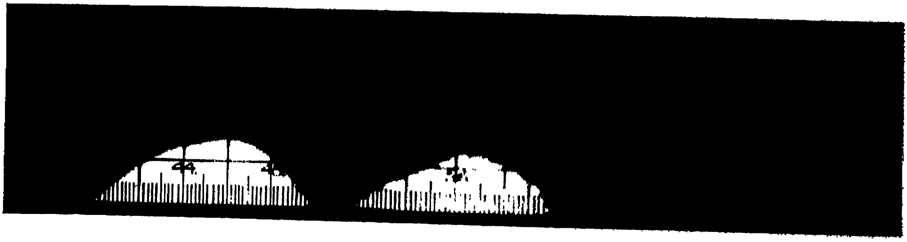


0.02 mg. dye per 100 cc. emulsion

Fig. 403. Effect of dye concentration on [illegible] produced by a thiacarbocyanine



4 mg. dye per 100 cc. emulsion



0.1 mg. dye per 100 cc. emulsion

Fig. 404. Effect of dye concentration on [illegible] produced by another thiacarbocyanine.

of an aqueous solution of the dye saturated with potassium bromide and, presumably, containing the dye in an aggregated form.

Schwarz[25] published an extensive paper on the different types of sensitization which may be produced by a single dye. His data for twelve carbocyanines, each having an alkyl group attached to the central carbon atom of the trimethine chain, show that the character of the sensitization by dyes of this very important group is quite dependent upon conditions. In every case, the maximum sensitivity occurring at the longest wave length may appear and disappear with change of concentration or emulsion type. Between optimum sensitization and disappearance of this maximum, the contrast in this region may fall to very low values, indicating that sensitization of a few grains of the emulsion is different from that of the rest. According to Leermakers, Carroll, and Staud, the long wave length maximum appears at a high concentration of dye and disappears at low concentration; and some of Schwarz's results may be due to changes in concentration of dye at the surface of the grains, since in some cases he used fine-grain emulsions with much surface and in other cases, coarse-grain emulsions. Schwarz demonstrated that digestion of the emulsion containing the dye aids the appearance of the long wave length maximum, and in some cases digestion may be a more important factor than concentration. This is presumably due to an orientation of the dye molecules during digestion and may be expected to apply especially to those cases discovered by Sheppard, Lambert, and Walker[21] (p. 1077) in which the adsorption of the dye proceeds slowly. In all cases cited by Schwarz or observed in the Kodak Laboratories, the maximum which is sensitive to concentration is at 25 to 80 mμ toward the long wave length side of the next maximum, and it is also sharper than the "low concentration" maximum. There is no case corresponding to Scheibe's observation of new maxima in solutions appearing at shorter wave lengths with increasing concentration. It is noteworthy that 3,3′-diethyl-9-methylthiacarbocyanine and 3,3′-dimethyl-9-ethylthiacarbocyanine have identical absorptions in methanol solution and show some similarity in what Schwarz calls their "first type of sensitization" but are quite different in the second type. Schwarz states that this second type of sensitization is common to carbocyanines substituted in the central position of the trimethine chain and also cites two cases of 2′-cyanines, but he found no case among carbocyanines unsubstituted in the chain. Experience in the Kodak Laboratories agrees with this and indicates that only a small fraction of all sensitizing dyes is capable of such notable variation in sensitization, and all of these are strong sensitizers. The explanation of the behavior of these variable sensitizing dyes must lie in the state of aggregation of the dye molecules when adsorbed to the silver halide.

THE ORIENTATION OF ADSORBED DYE MOLECULES

Only the first monolayer is important for actual sensitizing, since optimum sensitizing is achieved before the commencement of a second layer. The question arises of the orientation and packing of the dye molecules of the first layer upon the surface of the crystal. All the atoms in the resonance chain (of conjugated double bonds) may be assumed to lie in one plane, since only so could their valence shells be approximately regular tetrahedra in both extreme phases of the resonance. From data on atomic radii, bond distances, and angles in analogous compounds, M. L. Huggins[21] computed the approximate areas occupied (in close packing) for a carbocyanine dye and for erythrosine (*a*) for flat molecules, (*b*) for molecules on edge, and (*c*) for molecules on end. These values do not take into account specific effects of the arrangement of ions in the crystal surface upon the packing of the dye molecules. In a surface covered by dye ions, the distance between Br^- ions (for silver bromide) may be assumed to be the same as in the crystal (4.07 A). The area per Br^- in an octahedral (111) face is, then, $(4.07)^2 \times \frac{\sqrt{3}}{2} = 14.34$ A².

TABLE LXXXVIII

	Average Area for Close Packing	
	A Carbocyanine	*Erythrosine*
(*a*) Flat	140 A²	132 A²
(*b*) Edge-on	58	78
(*c*) End-on	26	75

Huggins calculated various possible unit cells in the surface layer and therefrom the number of Br^- ions per dye ion either in register with Br^- ion layer or closely packed. Values for other dyes may be calculated similarly.

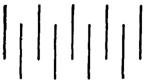
TABLE LXXXIX

			Number of Br^- *per Dye Ion*	
			In Register with Br^- *Layer*	*Closely Packed*
A carbocyanine	(*a*)	Flat	16 ~ 12	9.5 ~ 10
	(*b*)	Edge-on	4 or 5	~ 4
	(*c*)	End-on	2 or 3	1.8–1.9
Erythrosine	(*a*)	Flat	10 ~ 9	9.2
	(*b*)	Edge-on	6	5.5
	(*c*)	End-on	6	5.2

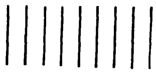
The experimental results are not quite unambiguous—the figures vary between three (page 1063) and ten (page 1069) bromide ions per dye molecule; the latter figure is supported by the most complete data. Sheppard gave as the most probable values for the cyanine dyes 4–6 bromide ions per dye ion adsorbed, which would indicate vertical edge-on piling of the dye molecules. The figure of 10, from the data of Table LXXXVII, corresponds to closely packed flat adsorption. For erythrosine the value was 8–14 bromide ions, corresponding to flat adsorption; but some further study is required in this case.

A conception of the arrangement of cyanine dye molecules adsorbed to silver halide was deduced from adsorption experiments by Sheppard[1] and Sheppard, Lambert, and Walker.[21] As already stated, they concluded that the cyanine dyes were adsorbed edge-on by the ionizable hydrophile nitrogens (or corresponding groups). The molecules have a *dorsi-ventral* character such that the hydrophobic back has no affinity for water, and the adsorption is generally irreversible. By virtue of this orientation, in close packing, packets of parallel planar molecules are formed, like packs of cards edge-on with an interval of about 3.5 A between the molecules (or dye cations). These packets were regarded as constituting the "aggregates" of Leermakers, Carroll, and Staud and the "nematic" phase of Jelley and as being responsible for the variable absorption and sensitizing bands of the dyes studied by Schwarz[25] and by Leermakers, Carroll, and Staud.

Jelley[8] gave evidence from birefringence and dichroism that in the case of the pseudocyanines, the new absorption band was associated with the formation of a mesomorphic, probably nematic, phase, and that the absorption corresponded to a transition parallel to the axis of the filaments. Scheibe[7,26] adduced similar and further evidence for "reversible polymers" as filamentous aggregates of dye cations. From adsorption experiments on mica (Muscovite), he obtained a picture of the adsorbed dye similar to that of Sheppard, of orthogonally oriented, parallel-piled cations, with an interval of $\sim$3.7 A; but he concluded that they formed staggered arrays:



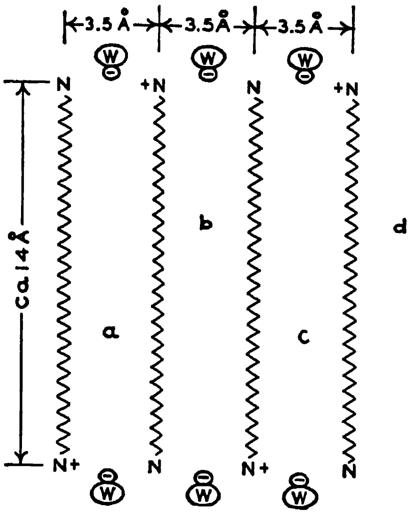
, RATHER THAN



He also gave evidence that the new oscillation must be parallel to the axis of the filament and perpendicular to the plane of the component molecules. While Scheibe's results establish the character of the cation aggregation in the new phase, they do not completely specify the conditions for the new absorption band. Leermakers, Carroll, and Staud showed that the absorption bands of dyed silver bromide were affected reversibly by moisture. This was confirmed by Sheppard, Lambert, and Walker; they found further that while adsorption from alcohol to the molecular state was irreversible, the aggregate phase was desorbed by alcohol and redeposited as the molecular phase, but in the presence of water vapor the aggregate phase was produced again.

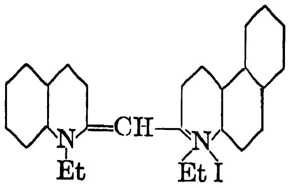
The importance of water for the new absorption band of pseudocyanines was also observed by Scheibe and by Jelley, who obtained in addition evidence for the existence of slightly different *hydrated* mesomorphous and crystalline states.

At least two factors, then, are necessary for the aggregate absorption band; a structure of *planar* molecules arranged in parallel card-pack fashion, at intervals of 3.5 A, and hydration. The following provisional model is suggested by Sheppard: Suppose that the nitrogen atoms are in the plane of the paper and the dye cations are perpendicular to this plane and parallel to each other:

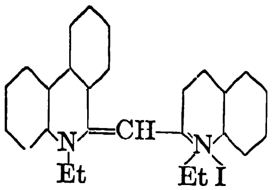


The distance between is ~3.5 A. Then, it is further supposed that water molecules between the N-atoms of a doublet afford replaceably mobile electrons which permit resonance, perpendicular to the molecule, of $>\overset{+}{N} \overset{\circ}{\rightleftharpoons} N<$. This is repeated by alternate pairs and furnishes a ground and upper state determining the spectral position of the new band. The active cells are alternate with similar inactive ones; hence, the band strength grows with length of filament, but the wave length does not change.

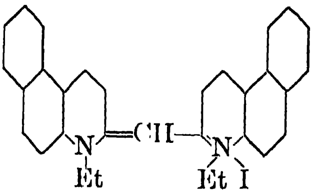
Sheppard considers that the most important evidence for the necessity for planarity in the molecules of dyes having sensitizing power is supplied by the study of two isomeric pairs of cyanine dyes derived from β-naphthoquinoline and phenanthridine, respectively. These were prepared by Brooker and Keyes and have the formulas:



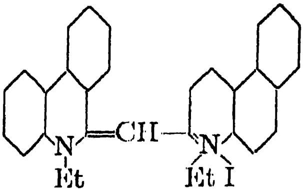
(*a*)



(*b*)

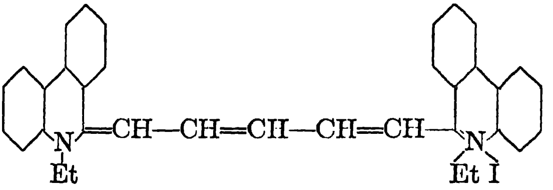


(c)



(d)

Brooker and Keyes observed that dyes (a) and (c) are sensitizers, while (b) and (d) do not sensitize.[27] This was confirmed by Leermakers, Carroll, and Staud, who observed adsorption of all four dyes to emulsion grains, with normal absorption of light, as determined by the reflectance of the dyed silver halide. Sheppard, Lambert, and Walker found that the adsorption rates of the non-sensitizing isomers in the presence of gelatin are considerably lower than that of the sensitizers, but all the equilibrium values agree well with calculations from the areas of the dye molecules. The adsorption data, then, do not indicate any difference between the sensitizing and non-sensitizing isomers. A difference was found in the steric impedance which prevents the non-sensitizing isomers from assuming a planar form. From the formulas for these isomers using correct bond angles and interatomic distances, it can be seen that complete planarity of the molecule is not possible in case (b) or (d) unless the 3,4-benzo radical is brought within a distance of approximately 1.7 A of the opposite quinoline or β-naphthoquinoline group. The formulas of other non-sensitizing cyanine dyes derived from isoquinoline[28] and from 5-methyl-acridine[29] are also nonplanar. However, Brooker* has prepared the phenanthridine dye



which was found to be devoid of sensitizing properties. There is no reason why this dye should be nonplanar, as the phenanthridine nuclei are well separated and steric hindrance does not occur. This indicates that some factor other than nonplanarity may deprive a cyanine dye of sensitizing power.

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* L. G. S. Brooker, private communication.

THE PHOTOLYTIC PROCESS WITH OPTICALLY SENSITIZED SILVER HALIDES

The photolytic process in a photographic emulsion seems to take the same course whether the light is absorbed directly by the silver halide or the light of longer wave lengths is absorbed by a sensitizing dye.[30] Evidence of the same primary process—the release of an electron—is given by the photovoltaic effect which is produced in dye-sensitized emulsions by the light absorbed by the dye, in the same way as by blue light in unsensitized emulsions (Chapter IV, p. 176). The parallelism between photolytic and photographic processes which was found to be characteristic for unsensitized emulsions is equally valid in sensitized emulsions. Sheppard, Lambert, and Walker[31] added isomeric cyanine dyes to silver bromide, one of the dyes being a sensitizer and the other a nonsensitizer, and compared the photolytic yields of silver. Photolysis by the nonsensitizing dye was negligible, while with the sensitizing dye a normal amount of silver was produced. The close relation between the photographic and the photolytic reactions for light absorbed by the sensitizing dye is further shown in Figure 405. The curve for the silver produced photolytically is very similar in shape to that for sensitivity. The maxima of both occur for nearly the same amount of dye adsorbed at the surface.

The measurement of the absorption of light by the dye is a serious difficulty in determining the amount of silver corresponding to the absorption of a given amount of energy by sensitized silver halide. Sheppard, Lambert, and Walker[32] found that the value for the initial quantum equivalent varied from 0.78 to 1.28, with an average value of 1.14, which suggests that for the reaction

$$D^{\mathrm{Ag}^+}_{\mathrm{Br}^-} + h\nu = D + \mathrm{Ag} + \mathrm{Br},$$

the quantum equivalent is unity. This agrees with the results obtained by a number of workers for unsensitized silver bromide (Chapter IV).

Two hypotheses as to the actual mechanism of optical sensitizing are possible: That the dye itself is changed by the action of light and, in turn, reduces the silver halide; or that the dye transfers to the silver halide the energy which it absorbs but is not itself affected by it.

For very low exposures, the amount of dye needed was calculated by Eggert and Biltz[33] for an emulsion optimally sensitized for green. The calculated surface of the grains equals that of the adsorbed dye within the rather wide limits of error, indicating a monomolecular layer of dye. Exposure to green light sufficient to produce a developed density of 0.1 above fog corresponded to an average of one quantum per grain absorbed by the dye. In a random distribution of such an exposure, five per cent of the grains would absorb three quanta, and one per cent, four quanta. Not more than five per cent of the grains were made developable, so that under these conditions, the most sensitive grains were made developable by three to four quanta. As an average grain had adsorbed 7 × 10^5 molecules of dye, only a small fraction of the dye molecules could have functioned in the exposure.

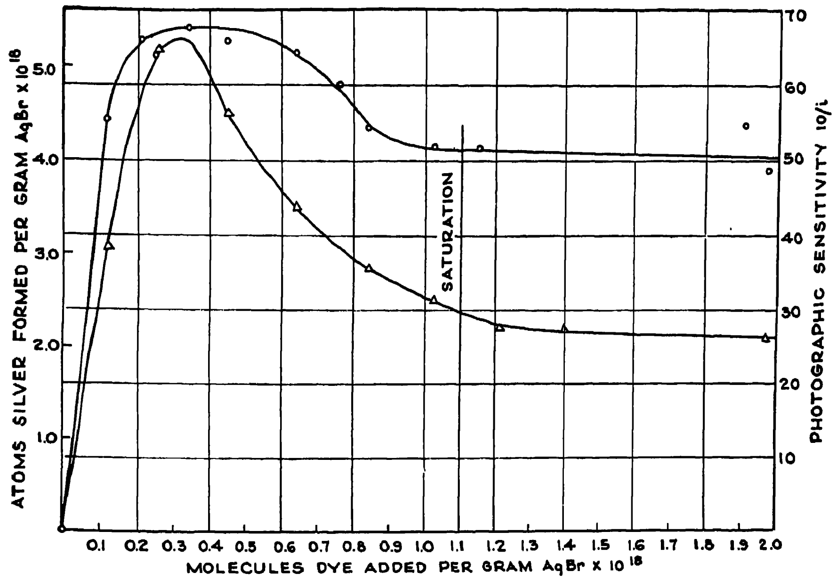

FIG. 405. Relation between the photographic and the photolytic reactions for dye-sensitized silver halide.

For high exposures, Lescynski[34] determined the amount of photo-silver formed by a given exposure to light of pure silver bromide emulsions to which erythrosine had been added. The silver produced by an exposure for about the maximum yield compared with the amount of dye added showed that about twenty silver atoms were formed for each molecule of dye present. Lescynski's observations were confirmed by Tollert,[35] who pointed out that only about 15 per cent of the erythrosine added to the emulsion was adsorbed to the silver bromide under the experimental conditions used. He observed that the silver formed increased to a maximum, at which point about sixty atoms of silver were formed for each molecule of erythrosine adsorbed.

Bokinik and Iljina,[22] who carried out a similar investigation, used a silver bromide hydrosol of ultramicroscopic particles stabilized by a slight excess of bromide ions instead of the emulsions used by Tollert. They found that from four to fifteen atoms of silver were produced per molecule of dye adsorbed, depending upon the exposure. These results accord with the idea that the dye itself does not change under the action of light but merely passes on the absorbed energy to the silver halide. A direct photochemical reaction of the dye would only be possible if the dye were regenerated as it was decomposed or if the dye were decomposed with such an excess of energy that a chain of reactions was started. The latter hypothesis is excluded by the fact that approximately one silver atom is produced per quantum absorbed.

Sheppard, Lambert, and Walker[32] investigated the action of light on dyes adsorbed both to silver halide grains and to silver bromide hydrosols similar to those used by Bokinik and Iljina. The silver was determined either by direct analysis with iodine or by photoelectric photometry as proposed by van Kreveld and Jurriens.[36] The precision of this latter method is given as fifteen micrograms of silver. It was found that erythrosine is destroyed progressively upon exposure, whether the light is that absorbed by the dye or is blue light absorbed by the silver bromide. From one to two atoms of silver are produced for each dye molecule destroyed. This suggests that the destruction of the dye is due to the bromine released upon exposure, which was confirmed by the use of halogen acceptors. In the presence of acetone semicarbazone, or phenol, the dye was not destroyed, although silver was still produced. The function of a halogen acceptor, however, in protecting the dye was found to be less simple than originally assumed. The slow addition of a dilute solution of bromine to a solution of dye containing a halogen acceptor produced discoloration. If the addition was discontinued as soon as the solution was discolored, the color returned and the dye was recovered unchanged. The dye was regenerated also if a solution of the decolorized, brominated dye was added to a halogen acceptor; and, in the same way, brominated dye added to a silver sol was regenerated with the production of silver bromide.

Thus, there are still two possibilities for the action of a dye in sensitizing: The absorbed energy may be transferred directly from the dye to the silver halide without any primary change in the dye, or the dye itself may be decomposed with the dissociation of the silver bromide as a secondary reaction and regeneration of the dye. There is at present insufficient experimental evidence for a decision between the two possibilities, but some light may be thrown upon the subject if it is considered from the standpoint of the Gurney-Mott mechanism for the production of the latent image (Chapter IV). The absorption of light by a dyed silver halide grain is followed by the liberation of an electron which moves through the crystal until it is trapped in a deformation of the lattice. The trapped electron neutralizes the silver ion, reaching the same spot, and converts it into a silver atom; but whereas with unsensitized silver bromide the electron is supplied by a bromide ion after absorption of a light quantum, the bromide ion being converted into a bromine atom, the origin of the electron in the *sensitized* reaction is not known. The liberation of an electron can be attributed either to the dye molecule after absorption or to the bromide ion to which the dye transfers the energy received by the absorption of light. Such a transfer of energy without radiation is well known and has been discussed extensively.[37] The ejection of an electron from the dye molecule involves the transfer of an electron from a bromide ion, which liberates a bromine atom and regenerates the dye. The bromide ion seems to be essential, however, for the sensitizing action of erythrosine, as was shown by Sheppard, Walker, and Lambert. Although silver erythrosinate has the same absorption spectrum as silver bromide dyed with erythrosine (page 1060), it does not show the same photolytic effect. An exposure which produced a large amount of silver from silver bromide dyed with erythrosine, and liberated an equivalent amount of bromine, produced no appreciable liberation of silver in silver erythrosinate. Thus, the photochemical effect depends upon the dye and the bromine ion in association.

An illustration of the possible mechanism is given in Figure 406. The silver bromide lattice is represented in the usual way

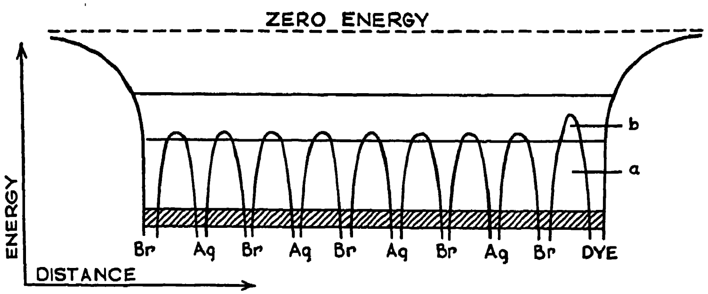

FIG. 406. Energy levels of electrons in dye-sensitized silver bromide.

by the energy curves of the silver bromide, and the energy levels of the electrons in their normal positions are located in the lower band. To raise them to the conductance level, the absorption of a sufficiently great quantum of energy by the silver bromide itself is required. At the surface, however, a dye electron can be raised from level *a* to level *b* by the absorption of a smaller quantum. The electron is now free to move in the conductance band, while the adjacent bromide ion transfers its electron to level *a*, the necessary energy for this transfer being supplied by the close coupling between the dye and the bromide ion. Alternatively, the electron may fall back from level *b* to level *a*, while the energy is transmitted by resonance to the adjacent bromide ion, which, again, by using the energy of coupling, may transfer the electron into the conductance band. This transfer of energy could not take place over any appreciable distance in view of the necessary supplementary energy, which can be provided only from a coupling with an adjacent particle.

It is seen that there is no essential difference between the two courses considered and that the essential change is the same, whether the electron from the dye is liberated in the conductance band or the electron from the bromide ion is transferred to the conductance band; but both views assume that energy is drawn from the coupling forces. The importance of these coupling forces for sensitizing is connected with the importance of the orientation of the dye molecules on the surface of the silver halide crystals discussed previously.

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